FINAL REPORT ON NASA COOPERATIVE AGREEMENT NCC3-286

Alkali Layered Compounds Interfaces for Energy Conversion and Energy storage

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**The total approved budget for all three years was $ 503.645
(CAU Budget No : 243604)**

**Dr. Chris A. Papageorgopoulos
Surface Physics Laboratory
Department of Physics
Clark Atlanta University
223 James P. Brawley Drive
Atlanta, Georgia 30214**

**Submitted To
National Aeronautics and Space Administration
Lewis Research Center
Contracts Support Branch
Attn: Grants Officer
Mail Stop 500-315
Cleveland, Ohio 44135**

* NASA approved an extension from 01/ 20 95 to 06/ 30/ 96

YEAR ONE

TOTAL (YEAR ONE)   **$167,266**

During Year One, I brought a complete new ultra-high vacuum (UHV) system equipped with a specimen manipulator, an Ar+ ion sputterer, a low energy electron diffraction (LEED) system, an Auger electron spectrometer (AES), a work function (WF) measurement device with a Kelvin probe and related accessories. The total cost of these items is approximately $170,000. The UHV system with the specimen manipulator, Ar+ ion sputterer and related accessories was obtained through other sources, totaling approximately $100,000. In addition to the above surface analysis techniques of LEED, AES, WF, and some accessories such as thermocouples, Ta, Ni and W wires, Ta foils of different thicknesses, pure gases, etc., were also purchased through the present grant (within the equipment budget).

On July, 1993, I visited the Photovoltaic Laboratory at NASA Lewis Research Center, where I gave a talk on "Alkali Adsorption on Layered Compounds". After extensive discussions with the staff, it was agreed that the thrust of our research efforts should be redirected to support pressing problems within the Photovoltaic group. We agreed specifically to study the *Adsorption of chalcogenides on Si and III-V compound semiconductors.*

On September 1993 I started receiving the ordered equipment; the UHV system and surface analysis techniques; an Auger electron spectrometer (AES), a Kelvin probe for work function (WF) measurements and a low energy electron diffraction (LEED) system. By the end of the year 1993 all the purchased equipment were put together, and the UHV system was brought to acceptable operating condition.

Much of the necessary equipment, however, was not available such as voltmeters, power supplies, an oscilloscope, chart recorders, computers, liquid nitrogen and other pieces. For a few days a week, we borrowed meters from the students' laboratory at Clark Atlanta University. The Photovoltaic group at NASA Lewis Research Center gave us some specimens of Si(100). In addition, Professor M. Kamaratos came from Greece on four-month sabbatical, and the first Master's Degree graduate student, Aris Papageorgopoulos, joined the group. And we thus began the proposed investigation.

In the meanwhile, the continuation proposal for Year Two had been approved.

YEAR TWO

TOTAL (YEAR TWO) $181,511

During Year Two, we ordered a scanning tunneling microscope (STM) fro $116,000, a quadrapole mass spectrometer, power supplies, a computer, a chart recorder, micro-voltmeters, a thickness monitor, an evaporator with its power supply (for GaAs and InP deposition), and related accessories. The total cost of these items was approximately $175,000. Most of the items, other than the STM and some accessories, were obtained through other sources totaling approximately $55,000.

Meanwhile, according to the collaboration agreement with the Photovoltaic group at NASA, we started the systematic study on the adsorption of chalcogenides on Si and III-V compound semiconductor surfaces. The study took place in the UHV with the available techniques of LEED, AES and WF measurements.

Specifically, we started with in in-situ adsorption study of elemental S on Ni(100). I would like to note that this is the first time that elemental sulfur, as opposed to sulfur compounds such as H_2S, is deposited at RT. This innovation supports a preliminary experiment with a prototype substrate such as Ni(100). The knowledge of the behavior of S on Ni is of particular interest due to the poisoning effects of S on catalytic reactions occurring on Ni surfaces. The results have been published in the Journal of Surface Science (see reference 1).

Next, we continued with the study of : "Adsorption (passivation) of elemental S on Si(100)2x1 Surfaces". This study was also part of the thesis of Aris Papageorgopoulos. Part of the results have been presented: at the 15th European Conference of Surface Science, ECOSS-15, September, 1995, Lille, France, with the title "Adsorption of elemental S on Si(100)2x1 surfaces", Aris Papageorgopoulos, M. Kamaratos. The same work with the same title has been accepted for publication by the Journal of Surface Science (reference 2).

Additional results of S on Si(100)2x1 surfaces were presented at the Mat. Res. Soc. Meeting, December, 1995, Boston, Massachusetts, with the title "Passivation of Si(100)2x1 surfaces with elemental sulfur", Aris Papageorgopoulos. This paper has also been accepted for publication in the Proceedings of Material Research Society Journal (reference 3).

After completion of the study of S on Si(100)2x1 surfaces, the results have been submitted to Physical Review B (reference 4).

Meanwhile, at the end of the second year, we received the STM and the quadrapole mass spectrometer, which we started to install.

In the mean time, the continuation proposal for Year Three has been approved.

YEAR THREE

TOTAL (YEAR THREE) $154,868

During this year we mounted the Scanning Tunneling Microscope (STM) on the existing UHV system. Then we tried to get familiar with the specific type of STM and bring it to acceptable operating conditions.

This year we bought a Hemispherical Analyzer for XPS-UPS measurements for $81,250, which is mounted to a new UHV system, which is specially designed for XPS-UPS measurements. The UHV system has been obtained through other sources.

Now going back to research, the investigation continues with the adsorption of Cs (alkali) on S-covered Si(100)2x1 surfaces. This was also the second part of Aris Papageorgopoulos' thesis. The first results have been submitted for publication to Journal of Surface Science (reference 5).

Subsequent results of Cs on S-covered Si(100) surfaces have been presented to the International Conference on the Structure of Surfaces, July 8, 1996 (Aix-en Provence, France). The title of this work was: "The behavior of Cs on S-covered Si(100)2x1 and Si(100)1x1 surfaces". The same paper, with the same authors, has been submitted to Surface Physics Review (reference 6).

The research activities continued with the adsorption of S on Cs-covered Si(100) surfaces. This work has been completed, it will appear in the thesis of our second graduate student, Adero Corner. The most important results of this work will be submitted for publication.

Presently, the third graduate student, Dwight Mosby, is working with the STM system and specifically he tries to confirm the proposed structure models of S and Cs on Si(100) surfaces.

In the near future, we are going to continue with GaAs and InP substrates.

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   Surface Sience 352-354 (1996) 364-368

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4. Adsorption of elemental S on Si(100) 2x1: surface reconstruction
   Aris Papageorgopoulos, Adero Corner, M. Kamaratos, C. A. Papageorgopoulos
   Submitted for publication to Physical Review B.

5. Adsorption of Cs on S-covered Si(100) surfaces
   Aris Papageorgopoulos, D. C. Papageorgopoulos
   Submitted for publication to Surface Science.

6. The behavior of Cs on S-covered Si(100) 2x1 and Si(100) 1x1 surfaces
   Aris Papageorgopoulos, Dwight Mosby Jr, C. A. Papageorgopoulos
   Submitted for publication to Surface Physics Review.

Ref. 1

Adsorption of elemental S on Ni(100) surfaces

C.A. Papageorgopoulos [*,1], M. Kamaratos [1]

Department of Physics, Clark Atlanta University, James P. Brawley Drive at Fair Street S.W., Atlanta, GA 30314, USA

Abstract

We have studied the adsorption of elemental S on Ni(100) surfaces by LEED, AES, TDS and WF measurements in UHV. We compared the measurements to those of reported investigations, most of which used H_2S as sulfur source. The elemental S, at room temperature, is grown on Ni(100) in a layer by layer mode. Sulfur forms the $p(2 \times 2)$, initially, and subsequently the $c(2 \times 2)$ structure at the completion of the first S layer. The second layer is disordered. These findings are in contrast with most of the published papers which report that the S on Ni(100) saturates in the first layer, its sticking coefficient decreases drastically and it does not desorb before 1200 K. Deposition of S, at RT, increases the work function of Ni by 0.25 eV. Heating before the desorption temperature (1100 K) of S causes: (a) a rearrangement of Ni atoms with a possible diffusion of Ni from the bulk to the surface, having the tendency to interact with the S overlayer and (b) an increase of the WF change close to 0.4 eV, the value reported after the exposure of Ni(100) to H_2S and subsequent heating. The AES and WF variation are related to a recently reported difference in electronic structure between the $p(2 \times 2)S$ and $c(2 \times 2)S$ structures.

Keywords: Auger electron spectroscopy; Low energy electron diffraction (LEED); Nickel; Silicon; Thermal desorption spectroscopy; Work function measurements

1. Introduction

The adsorption of sulfur on nickel surfaces has been extensively studied in the past. The knowledge of the behavior of S on Ni is of particular interest. This is due to poisoning effects of S on catalytic reactions occurring on Ni surfaces [1–3], and the recent finding that sulfurization treatment is very important in the passivation of different surfaces [4–6]. The adsorption sites of S atoms, the changes of the electronic properties of the surface, and the substrate relaxation after S deposition on Ni surfaces

have been studied by a variety of surface analysis techniques [7–10].

Despite the amount of research, there are still questions about the S–Ni system. Most of the S adsorption studies, up to now, have taken place with the exposure of the substrate surface to H_2S gas. To remove the H_2 from the surface the substrates were heated to equal or greater than 200°C [10–15]. The role of hydrogen and subsequent heating on the growth mode of S alone on Ni(100), however, is not known. For a detailed understanding of the adsorption kinetics of S on Ni surfaces at room temperatures and lower, it is important to deposit elemental sulfur.

In this work we evaporate elemental sulfur on Ni(100) surfaces. We study the sample using low

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[*] Corresponding author.
[1] Permanent address: Department of Physics, University of Ioannina, P.O. Box 1186, GR-451 10 Ioannina, Greece.

energy electron diffraction (LEED), Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and work function (WF) measurements. The measurements suggest kinetics of S and Ni interaction during S deposition at room temperature (RT) and subsequent heating of Ni(100) substrates which are reported for the first time.

2. Experimental

The experiments were performed in an ultra-high vacuum chamber ($p < 10^{-10}$ Torr), equipped with a cylindrical mirror analyzer (CMA) for AES and EELS measurements, a quadrupole mass spectrometer (QMS) for TDS measurements, a Kelvin probe for WF measurements and a LEED system.

Elemental sulfur was evaporated by thermal dissociation of MoS_2 single crystal flakes mounted on a tungsten filament. During dissociation of MoS_2 the Mo remained on the tungsten filament, while S was evaporated. The Ni(100) substrate was cleaned by Ar^+ bombardment (1 kV, 5 μA) for 20 min and subsequent annealing at about 1000 K. This cycle was repeated several times until the AES peak heights of the main impurities (carbon and sulfur) were almost negligible. The temperature of the sample was measured by a Cr–Al thermocouple calibrated with an infrared pyrometer in the range of 900–1200 K.

3. Results and discussion

Fig. 1 shows the Auger peak-to-peak heights (Ap–pH) of S(151 eV), Ni(61 eV) and their Auger peak-to-peak height ratios, S(151 eV)/Ni(61 eV), in correlation with the LEED patterns, as a function of doses of S deposition. It is obvious, from this figure, that the S/Ni ratio increases linearly with increasing number of S doses, with a break (slope change of the S/Ni ratio versus S doses curve) occurring at 13 doses. The peak-to-peak height of Ni(61 eV) decreases analogously with a break occurring at 13 doses of S. The peak-to-peak height of S(151 eV) also increases linearly with increased doses of S. The latter, however, forms two breaks. The expected at 13 doses, and an extra one at 6 doses of S deposi-
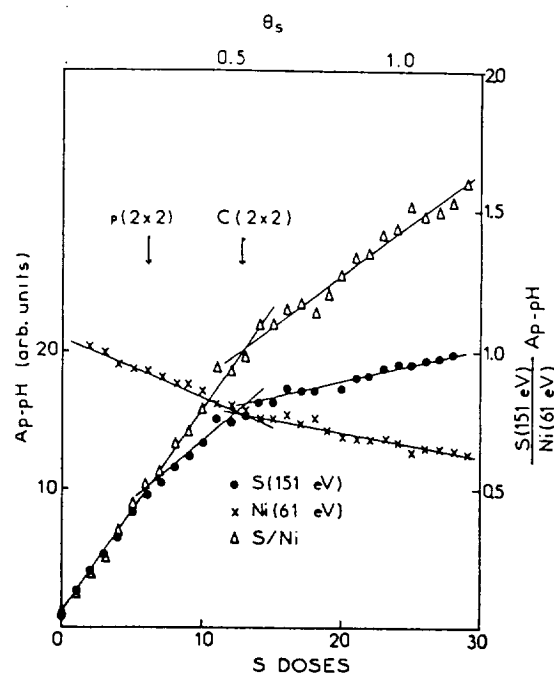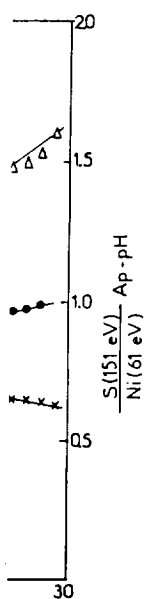

Fig. 1. Auger peak-to-peak height (Ap–pH) of S(151 eV), Ni(61 eV) and their Auger peak-to-peak height ratios, S(151 eV)/Ni(61 eV), in correlation with the LEED patterns, as a function of S deposition doses.

tion, with a smaller change of the slope than that at 13 doses.

The LEED observations show the well-known patterns of p(2 × 2) and c(2 × 2) with maximum spot intensities at 6 and 13 doses of sulfur, respectively. We assume that the corresponding S coverages, Θ_S, at the completion of the above structures are 0.25 and 0.5 monolayers. These results suggest that the sticking coefficient of S on Ni(100) is constant, at least up to 13 doses ($\Theta_S = 0.5$). Previous measurements, with H_2S as the sulfur source, have shown that the sticking coefficient of S on Ni(100) surfaces decreases drastically with S deposition [10,16–18]. Partridge et al. specifically, have reported that the p(2 × 2) and c(2 × 2) sulfur overlayer structures were obtained at room temperature, by dosing the clean Ni surface, correspondingly, with 1 and 50 L of H_2S [10]. Hardergree et al. [11], also using an H_2S source, reported that the value of the S(152 eV)/Ni(61 eV) Auger peak-to-peak height ratio at $\Theta_S = 0.5$ was found to be 1.23, which was very close to the ~ 1.26 value reported in this work.

Blaszczyszyn et al. [12] used sulfur ampoules to deposit S on Ni wires (field emitters). From field electron microscopy (FEM), they obtained the information that the sticking probability of S on the Ni specimen was approximately unity. A correlation of this information with our LEED and AES measurements suggest that, for the first layer, 1 dose of S is about equal to 0.04 ML.

According to Fig. 1, after the completion of the $c(2 \times 2)S$ structure, the S/Ni ratio and the S(151 eV) peak-to-peak height continue to increase linearly with a smaller slope (break), even above 30 doses. The break indicates the growth of a second S layer. It is well known that these kind of breaks are characteristic of layer by layer growth. The substantial decrease in slope of the Auger curve of S during the second layer formation (Fig. 1), and the fact that we did not reach the completion of the second layer at the 30th S dose – approximately three times the quantity of doses required for the formation of the first layer – may imply that the sticking coefficient of S in the second layer is smaller than that of the first layer.

The formation of the second layer is consistent with the LEED observation that the deposition of S above 13 doses ($\Theta_S > 0.5$) causes an increase of the background in the pattern. The spots of the $c(2 \times 2)$ become diffused, which further suggests that the grown second layer of S is disordered. This finding, however, does not agree with most of the published results. These, latter, report that the saturation S coverage on Ni(100) is established at about 0.5 ML [16–18]. It is most likely, that the kinetics of adsorption and/or interaction of the deposited elemental S on the Ni substrate at RT are not quite the same as those during the exposure of the Ni to H_2S and subsequent heating [10,11,16–19].

The first (extra) break of the S(151 eV) Ap–pH versus S doses curve, at the completion of the $p(2 \times 2)S$ pattern (6 doses) may be attributed to a substantial difference between the $p(2 \times 2)$ and $c(2 \times 2)$ phases. We believe that this pertains to the significant change in the surface electronic structure of $c(2 \times 2)$, reported in the recently published STM measurements by Partridge et al. [10].

Fig. 2 shows, $\Delta\Phi$, the change of the work function (WF) during S deposition on Ni(100) surface. The WF increases with the increasing S coverage up
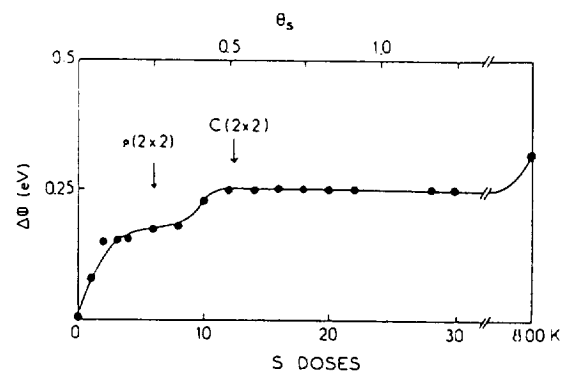

Fig. 2. Work function change, $\Delta\Phi$, during S deposition on Ni(100) surface.

to $\Theta_S = 0.5$, and remains relatively constant with further S deposition. At $\Theta_S = 0.25$ the WF curve forms a small plateau, with $\Delta\Phi = 0.17$ eV, and subsequently increases again up to $\Theta_S = 0.5$, where the WF levels off at $\Delta\Phi = 0.25$ eV. These values are less than those reported for the same S coverages on Ni(100) in other work. Specifically, Hardgree et al. measured $\Delta\Phi = +0.40$ eV at $\Theta_S = 0.5$ [11]. The initial plateau near the formation of the $p(2 \times 2)$ LEED pattern, and the subsequent abrupt increase of the WF with the growth of the $c(2 \times 2)$ has not been reported before. After reaching the final WF value the Ni substrate was heated to 800 K and the WF change increased to ~ 0.35 eV (Fig. 2). This value is very close to the saturation values measured after the exposure of the Ni(100) surface to H_2S and subsequent heating [11]. The abrupt increase of the WF during the transition from the $p(2 \times 2)$ to the $c(2 \times 2)$ phase may owe itself to a change in surface electronic structure [10].

Fig. 3 shows the variation of the Auger peak-to-peak height of the S(151 eV) and Ni(61 eV) peaks and their ratio S(151 eV)/Ni(61 eV) of nearly two layers of S covered the Ni(100) surface as a function of substrate temperature up to 1100 K. The experimental conditions did not allow us to go higher than 1150 K. As it is seen in this figure, the peak-to-peak height of the S(151 eV) Auger peak remained almost constant up to 1000 K. It started to decrease above this temperature by about one tenth of its initial height at 1100 K. The Ni(61 eV) peak-to-peak height, however, increased almost linearly from the beginning of the heating. This increase became more
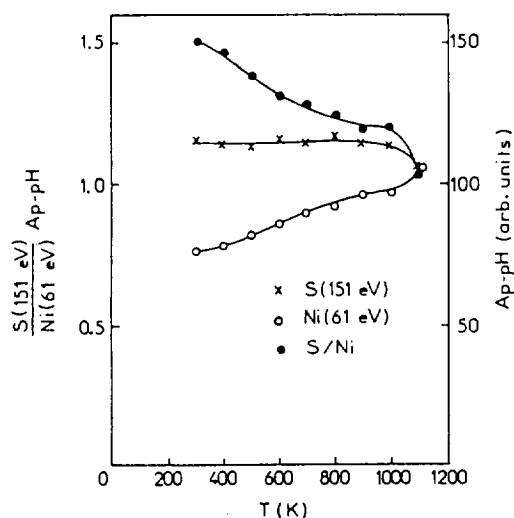
Fig. 3. Variation of the Auger peak-to-peak height of the S(151 eV), Ni(61 eV) peak and their ratio S(151 eV)/Ni(61 eV) of nearly two layers of S covered the Ni(100) surface as a function of substrate temperature up to 1100 K.

abrupt above 1000 K, where the S peak started to decrease. The S(151 eV)/Ni(61 eV) Auger ratio decreased in proportion to the increase of the Ni(61 eV) peak. It appears that sulfur started to leave the surface at about 1000 K. This is consistent with the thermal desorption measurements shown in the next figure. The unexpected continued increase of the Ni(61 eV) peak from the beginning of the heating, when the S was not yet removed from the surface may be attributed to a rearrangement of the surface. Most likely, heating provides the activation energy for the Ni atom to diffuse from the bulk to the surface. The diffused Ni interacts with the S atoms, possibly of the second layer, with the tendency to form a disordered overlayer of a sulfide. The diffusion should occur in a way that minimizes the masking of S atoms by the outgoing Ni atoms. The S atoms are smaller than those of Ni and diffusion of the latter in between the S atoms of the c(2 × 2)S, in the first layer, may cause an increase of the Ni Auger peak height. The behavior of elemental sulfur on Ni(100) is quite similar to that of O_2 on Ni(100). Adsorption of oxygen on Ni(100) at RT forms a c(2 × 2) with the completion of the first layer of oxygen and then a thin film of Ni-oxide [20].

At 1100 K the S/Ni Auger peak-to-peak ratio is reduced to about one, and the LEED pattern shows a

c(2 × 2) with sharp spots. This means that at 1100 K the second layer of S is desorbed while the first monolayer with the c(2 × 2) structure remains on the surface after heating to 1100 K. This is consistent with the following correlation of the TDS measurements and LEED observations.

Fig. 4 shows a series of S_2 (amu 64) of thermal desorption spectra for different amounts of S deposited on Ni(100) surfaces. The heating rate of desorption was constant for all spectra. There is a sharp peak in the 1050–1150 K range. This peak appears only for S deposition higher than 12 doses or $\Theta_S > 0.5$. The S (amu 32) exhibits the same behavior, but its TD peak is substantially smaller. After the heating up to 1150 K the LEED pattern shows a sharp c(2 × 2) as in the case of AES and LEED correlation during heating (Fig. 3). According to our knowledge, this peak has not been reported before. Most of the experimental publications on the S/Ni(100) system report that sulfur desorbed from Ni(100) at 1500 K. Specifically, Hardergree et al. [11] report that the chemisorbed sulfur resulting from
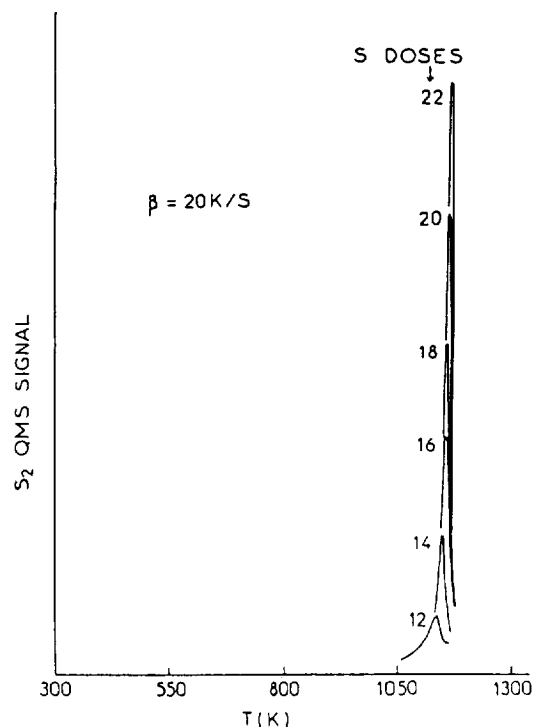

Fig. 4. A series of S_2 (amu 64) of thermal desorption spectra for different amounts of S deposited on Ni(100) surfaces.

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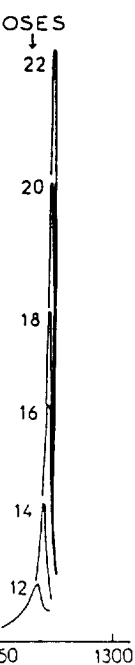
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H_2S dissociation did not desorb upon heating to 1200 K. Blaszczyszyn et al. [12] reported that sulfur desorbed from Ni only at temperatures above 1500 K. As we mentioned earlier, the latter authors used a Ni tip as a substrate and applied field emission microscopy (FEM). They related the desorption of S with the temperature (1500 K) of complete removal (cleaning) of sulfur from the surface.

The TDS measurements suggest that the binding of S on Ni(100) is characterized by two adsorption states: the known high energy (1500 K) [11,12] and the low energy ($\sim$ 1100 K) state. The high energy state is attributed to the first layer with the c(2 × 2)S structure, while the low energy state is due to the second layer of sulfur. The low energy TD peak of S might be due to a dissociation of a sulfide overlayer. We did not observe any TD peak of Ni–S complex other than that of S. Using a simple Redhead formula [21], and assuming a pre-exponential factor of 10^{13} s^{-1}, we calculated the binding energy of the second layer of S on Ni(100) ($\Theta_s > 0.5$), to be 3.5 eV. For the first layer the activation energy of desorption was found to be in the 4–4.3 eV range [10,22]. The areas under the thermal desorption peaks in Fig. 4 have been observed to increase linearly with increasing number of S doses. It is known that for constant heating rates, these areas are proportional to the adsorbate's coverage, and the slope of the areas under TD peaks versus S dose curve is proportional to the sticking coefficient. The linear increase of the peak areas in Fig. 4 with increasing number of S doses, therefore, suggests that the second layer of S on Ni(100) is deposited with a constant sticking coefficient.

4. Summary

We have used a correlation of LEED, AES, TDS and work function measurements in UHV to study the deposition of elemental sulfur on Ni(100) surfaces. We compared the measurements to those of reported investigations, most of which used H_2S as sulfur source.

Elemental S was grown on Ni(100), at RT, in a layer by layer mode. Sulfur formed, initially, a p(2 × 2) and subsequently a c(2 × 2) structure with the completion of the first layer, while the second layer

was disordered. When S is deposited on Ni(100) it appears in two adsorption states. The known high energy state at 1500 K, where S is completely desorbed from Ni, and the low energy state at $\sim$ 1100 K, with a binding energy of 3.5 eV, due to the desorption of the second S layer. The sticking coefficients of S in the first and second layers, respectively, were constant. These findings are in contrast with most of the published papers which report that the S saturates in the first layer, its sticking coefficient decreases drastically [1,16–18], and S does not desorb from the surface before 1200 K [12].

Heating of the S/Ni(100) system caused a rearrangement of Ni atoms near the surface. There was a possible diffusion of Ni outward, before any removal of S from the surface. Heating, most likely, provides the activation energy for Ni to diffuse from the bulk to the surface. There it may tend to interact with the S overlayer to form some sulfide. We found the final WF change, with S deposition on Ni(100) at RT, to be 0.25 eV. Subsequent heating to 800 K, however, increased the WF close to, 0.4 eV. This latter is the reported value after exposure of Ni(100) to H_2S, followed by heating to 300°C [11]. Finally, the AES and WF variations agree with the different electronic structure of the c(2 × 2)S structure as compared to the p(2 × 2)S [10].

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Adsorption of elemental S on Si(100)-2 × 1 surfaces

Aris Papageorgopoulos, M. Kamaratos [*,1]

Department of Physics and Center for High Performance Polymers and Ceramics, Clark Atlanta University, Atlanta, GA 30314, USA

Abstract

We have studied the adsorption of elemental S on Si(100)-2 × 1 surfaces by LEED, AES, TDS, and WF measurements in UHV. The adsorption of S at room temperature causes the surface restoration of the reconstructed Si(100)-2 × 1 substrate to its original bulk-terminated surface, Si(100)-1 × 1. The S adsorbate follows the substrate structures, i.e. it forms initially a (2 × 1) up to 0.5 ML and subsequently a (1 × 1). Above 1 ML, sulfur is imbedded into the Si bulk near the surface. The sticking coefficient of S on Si(100) surface is constant, $S = 1$, up to 2 ML. Deposition of S at RT up to 1 ML increases the WF of the surface by about 0.30 ± 0.05 eV. Above 1 ML, as the S is diffused into the Si bulk, the WF decreases. The TDS measurements show that S is desorbed as SiS molecule with a single TD peak near 585°C. This may indicate that the Si–S bond energy is greater than that of Si–Si which may be the dominant cause of the substrate restoration.

1. Introduction

Silicon as well as other semiconductors (GaAs, InP) have demonstrated great value, along with their importance in microelectronics and optoelectronics [1,2], as sources of power (solar cells) for space exploration [3].

The knowledge of the behavior of S alone on the above semiconductors and specifically on Si is very important because of the interest which has arisen with respect to the possibility of pretreating the surfaces of the semiconductors with S to protect and stabilize these surfaces against degradation which

may reduce their efficiency as solar cells or other devices [4,5].

In addition to the importance in applications, there is a recent rising scientific interest on the structural and electronic properties of chalchogen elements (S, Se) on Si(100)-2 × 1 surfaces. Theoretical calculations suggest that chalchogen adsorbates change the structure of the Si(100)-2 × 1 surfaces [6,7]. According to our knowledge, this does not agree with the up to-date relevant experimental results. More specifically, the Si(100) surface is easily reconstructed with a small amount of heating. The clean Si(100) surface shows a strong (2 × 1) reconstruction in the LEED pattern. This has been observed for the first time by Schlier and Farnsworth in 1959 [8]. It has been recently accepted by most researchers that dimers are the main building blocks of the reconstructed surface

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* Corresponding author. Fax: +30 651 45381.

[1] Permanent address: Department of Physics, University of Ioannina, P.O. Box 1186, GR-451 10 Ioannina, Greece.

of Si(100) [9]. The question, however, whether the dimers are symmetric or buckled remains unclear, as reported by Chadi [10]. Today, new evidence of asymmetric dimers is supported by most of the experimental [11–15] and theoretical [6,7] investigators who have worked on this problem. Kruger and Pollman [6] calculated that buckled dimers are energetically favored over symmetric ones by 0.14 eV per dimer [6]. The restoration of reconstructed semiconductor surfaces to their original bulk-terminated surface has been achieved, lately, by different adsorbates other than S on Si (100) [16–19]. Adsorption of S on clean Ge(100)-2 × 1 changed the (2 × 1) structure to (1 × 1). The system S/Ge(1 × 1) was regarded as an ideal terminated surface [20]. The same authors [21] have, experimentally, investigated the behavior of S on Si(100). They have not observed an ordered S adlayer. Moriarty et al. [22] reported, recently, that room temperature adsorption of sulfur resulted in the formation of an overlayer with the underlying Si(100) retaining the 2 × 1 reconstruction. They also mentioned that annealing of the S/Si(100)-2 × 1 surface to 325°C leads to the desorption of the sulfur overlayer and the appearance of coexisting c(4 × 4) and (2 × 1) surface reconstruction. In contrast to this report, theoretical studies performed by Kaxiras [7], and later by Kruger and Pollman [6], suggested that adsorption of group VI elements (S or Se) on Si(100)-2 × 1 can lead to restoration of the ideal bulk-terminated geometry on the semiconductor surfaces. From the above discussion it is apparently clear that additional effort on the study of S and Se on Si(100)-2 × 1 is necessary.

In this work we evaporate elemental sulfur on Si(100)-2 × 1 surfaces. The data suggest that the presence of sulfur adsorbate on the surface changes the surface structure of the Si(100)-2 × 1 substrate.

2. Experimental procedure

The experiments were performed in an ultrahigh vacuum chamber ($p < 10^{-10}$ Torr), equipped with a cylindrical mirror analyzer (CMA) for AES measurements, a quadrupole mass spectrometer (QMS) for TDS measurements, a LEED system, and a Kelvin probe for work function (WF) measurements.

Elemental sulfur was evaporated by thermal dis-

sociation of MoS_2 single crystal flakes mounted on a tungsten filament. During dissociation of MoS_2 the Mo remained on the tungsten filament, while S was evaporated. The Si(100) substrate was cleaned by Ar^+ bombardment at $E = 1$ keV for 40 min with an ion current of 10 μA. After bombardment the sample was heated to 1000°C by passing current through a 0.05 mm Ta strip, uniformly pressed between the sample and a Ta foil case. The temperature of the sample was measured by a Cr–Al thermocouple. The Si specimen was considered sufficiently clean when the Auger peak height ratios C(272 eV)/Si(92 eV) and O(512 eV)/Si(92 eV) were below 1%. The surface atomic density of 1 monolayer of S on Si(100) is considered equal to that of the outermost layer of Si, $N_{Si} = 6.8 \times 10^{14}$ atoms cm^{-2}.

3. Results

Fig. 1 shows the Auger peak-to-peak heights (Ap–pH) of the S(151 eV) and of the Si(92 eV) as a function of the number of doses of S deposited on clean Si(100)-2 × 1 surfaces at room temperature. These are in correlation with the observed LEED patterns which will be discussed later in this section. The Auger peak-to-peak height of S(151 eV), as seen in this figure, initially increases linearly with an increasing number of S doses. Near the 9th dose the curve forms a break (slope change of the S Auger peak height versus S dose curve). The S Auger peak height is increasing up to the 16th dose of our measurements where it forms a second break. The
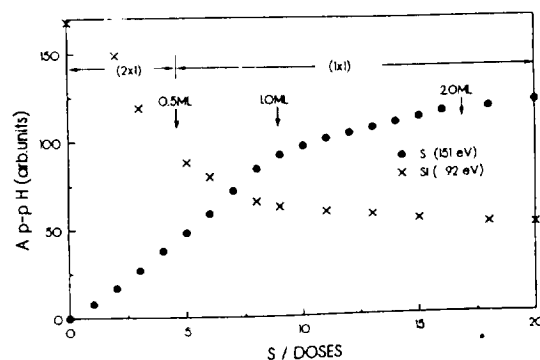

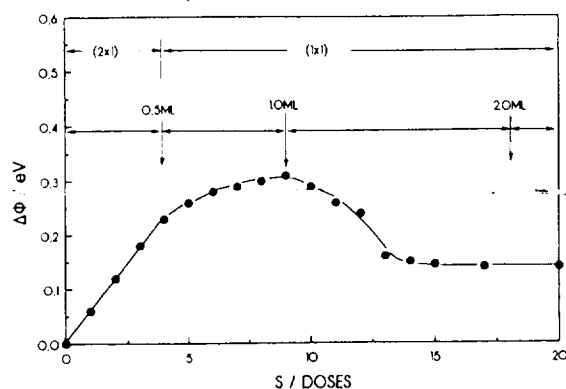Fig. 1. Auger peak-to-peak heights of Si(92 eV) and S(151 eV) versus S doses on clean Si(100)-2 × 1.

Fig. 2. Work function change versus sulfur doses on Si(100)-2×1 surface.

peak-to-peak height of Si(92 eV) decreases analogously with a break occurring at about 8 doses of S. Above the 16th dose the S(151 eV) peak height starts to level off, indicating that the sticking of S on the Si surface becomes negligible. During S deposition on the Si(100)-2×1 surface, the Auger Si(92 eV) peak is shifted with increasing number of S doses towards the lower energy by 1.5 eV up to the 16th dose of S. This is an indication of Si–S strong interaction and will be discussed further after the TDS measurements.

Fig. 2 shows the work function (WF) change versus the S doses on the clean Si(100)-2×1 surface at room temperature. These measurements are also in correlation with the LEED patterns during sulfur deposition. The WF increases initially linearly with increasing S coverage. Above the fourth S dose the slope of the work function curve becomes smaller. Near the 9th dose, the work function reaches its maximum value and subsequently starts to decrease as the number of sulfur doses increases. Above the thirteenth dose the decrease of the WF is very small, despite that the Auger peak height of S(151 eV) continues to increase (Fig. 1).

Next we will combine the above measurements with LEED observations. The clean Si(100)-2×1 surface shows a good, intense (2×1) LEED pattern. Initial deposition of S on this surface does not change the (2×1) structure. Above the fourth dose, the half-order spots become diffuse and the pattern changes to a (1×1) with its maximum intensity near

the 9th dose. Further S deposition increases the background, however, the (1×1) structure remains.

We believe that S on Si(100)-2×1 forms also a (2×1) structure, initially. The maximum intensity of the (2×1) pattern, near the 4th S dose, corresponds to 0.5 ML of S coverage. Above the 4th dose, both the Si substrate and the S adsorbate change to a (1×1) structure. The completion of the (1×1), near the 9th dose, corresponds to 1.0 ML of S, and coincides with the first break of the Auger curve (Fig. 1) and the maximum increase of the WF value (Fig. 2).

The same UHV system has been used previously with the same S-source, and about the same flux of S on Ni(100) [23]. The LEED observations showed the formation of a c(2×2) pattern close to the 12th dose of S on Ni(100). The density of the S overlayer, which produces the c(2×2) on Ni(100) is 8×10^{14} atoms cm^{-2} at 12 doses. At 9 doses the density should be about 6×10^{14} atoms cm^{-2}. This is very close to 6.8×10^{14} atoms cm^{-2}, which is the density of 1 ML of S on Si(100). Therefore, the completion of the S(1×1) structure on Si(100) at 9 doses is indeed about 1 ML of sulfur. It has been proposed that the initial sticking coefficient of S on clean Ni(100) is close to unity [24]. This implies that the initial sticking coefficient of S on Si(100)-2×1 is also one.

Thermal desorption spectra from S-covered Si(100) surfaces did not show any observable peak of S_2 (64 amu). Sulfur was mainly desorbed as SiS compound. Fig. 3 shows a series of SiS (60 amu) of thermal desorption spectra for different amounts of S deposited on Si(100) surfaces. The heating rate of desorption was constant, $b = 30$ K s^{-1}, for all spectra. There is only a single peak with its maximum value near 585°C. The areas under the TD peaks of SiS increase linearly with increasing number of S doses up to 16th dose of S, where, we believe, that the completion of the second S layer occurs. It is known that the slope of the areas under the TDS versus doses of a deposited adsorbate on a substrate is proportional to the sticking coefficient of the adsorbate. This, implies that the sticking coefficient of S on Si(100) surfaces is constant up to 2 ML, and subsequently becomes substantially smaller. Based on this we may assume that the drastic slope changes near the 9th dose of the Auger curve (Fig. 1) and the
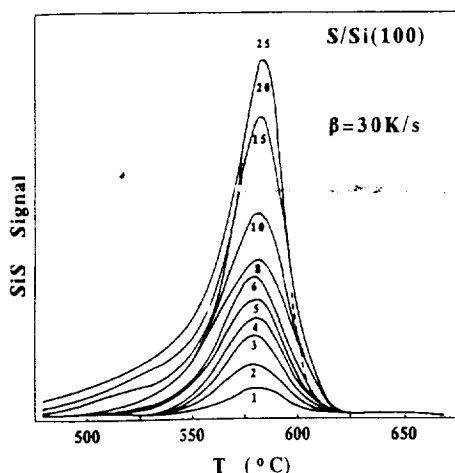
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Fig. 3. Thermal desorption spectra of SiS from S-covered Si(100) surfaces.

work function decrease (Fig. 2) are consistent with a submergence of the second S layer into the Si near the surface.

During heating of the S-covered Si(100) surfaces the Auger, LEED, and WF measurements follow their variations during S deposition in reverse.

4. Discussion

The current experimental LEED observations show very clearly that deposition of elemental sulfur on clean Si(100)-2 × 1 surfaces at room temperature changes the Si (100)-2 × 1 structure to Si(100)·1 × 1. This phase transition, is reported for the first time. We believe that the S adsorbate follows the substrate structures, i.e. it forms a (2 × 1) up to 0.5 ML and a (1 × 1) above this coverage.

The TDS measurements (Fig. 3) show that S is desorbed as SiS molecule. This indicates clearly that the S–Si bond energy is greater than that of Si–Si, which may indeed be the dominant cause of the substrate restoration to a Si(100)-1 × 1. It is important that the S coverage is greater than 0.5 ML in order to maintain the Si restoration. Our results of S adsorption on the Si substrate are in agreement with Kaxiras [7], and later with Kruger and Pollman's [6] theoretical calculations. According to their results

adsorption of S or Se causes the surface restoration of the reconstructed Si(100)-2 × 1 substrate to its original bulk-terminated surface. Kaxiras, in his report, considered different structures consisting of imbedding and mixing of the group-VI adatoms with Si substrate atoms. This is in agreement with the imbedding of the second S layer into the Si bulk. The author emphasizes, however, that the restored surfaces are stable against all of the considered alternative structures.

Besides the theoretical support [6,7] on the restoration of the semi-conductor surfaces to their original bulk-terminated geometry achieved by S and Se adsorbates, there are also several experimental results mentioned already in the introduction. Especially, Weser et al. [20] reported that S on Ge(100)-2 × 1 changed the (2 × 1) structure to (1 × 1) and that the S/Ge(100)-1 × 1 system was regarded as an ideal terminated surface. The same authors, however, have not observed any ordered S overlayer on the Si(100)-2 × 1 surface [21]. Recently, Moriarty et al. [22] reported that room temperature adsorption of S resulted in the formation of an overlayer on Si(100)-2 × 1, retaining the (2 × 1) reconstruction. They also report that annealing of S covered Si(100)-2 × 1 at 325°C leads to the desorption of the sulfur overlayer. As it is already mentioned, the complete removal of S takes place by heating the substrate to 650°C.

5. Summary

We have used a correlation of LEED, AES, TDS and work function (WF) measurements in UHV to study the deposition of elemental sulfur on Si(100)-2 × 1 surfaces. The adsorption of S at room temperature causes the gradual change of the reconstructed Si(100)-1 × 1. The S adsorbate follows the substrate structures, i.e. it forms initially a (2 × 1) up to 0.5 ML and subsequently a (1 × 1) structure. Above 1 ML, Sulfur is imbedded into the Si bulk near the surface. The sticking coefficient of S on Si(100) surface is constant, $S = 1$, up to 2 ML. Deposition of S at RT up to 1 ML increases the WF of the surface by about 30 ± 0.05 eV. Above 1 ML, as the S is diffused into the Si bulk, the WF decreases. The TDS measurements show that S is desorbed as Si–S molecule with a single TD peak near 585°C. This

may indicate that the Si–S bond energy is greater than that of Si–Si which may be the dominant cause of the substrate restoration.

Acknowledgements

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PASSIVATION OF Si(100)2x1 SURFACES WITH ELEMENTAL SULFUR

ARIS PAPAGEORGOPOULOS

Department of Physics and Center for High Performance Polymers and CeramicS
Clark Atlanta University, Atlanta, GA 30314, USA

ABSTRACT

Deposition of elemental S on Si(100)2x1 surfaces at room temperature changes the reconstructed Si(100)2x1 to its original bulk-terminated Si(100)1x1 surface. Sulfur forms initially a (2x1) on the Si(100)2x1 surface and subsequently a (1x1) on the Si(100)1x1. Above 1ML, sulfur is diffused into the Si bulk near the surface. The sticking coefficient of S on Si(100) surface is constant up to 2 ML. Deposition of S at RT up to 1 ML increases the work function of the surface by about .3$\pm$0.05 eV. Above 1 ML, as the S is diffused into the Si bulk, the work function decreases.

INTRODUCTION

Silicon and other semiconductors (GaAs, InP) are widely used in high-speed electronics, long-wavelength optical circuits (optoelectronics) [1,2] and, mainly in space technology, as solar cells (photovoltaics) [3]. Their efficiency, however, is reduced by radiation damage [4,5], and other causes which may change the surface composition. To prevent damage in the surfaces involved without reducing their efficiency the above semiconductors are pretreated with protective films. Recently, an interest has arisen with respect to the possibility of pretreating the surfaces of the above semiconductors with S and S-compounds to protect and stabilize them against the degradation [4,5].Working on a program related to the growth of protective films on photovoltaics, we felt that the knowledge of the behavior of S alone on the above semiconductors and specifically on Si is very important.

In addition to the importance in applications, there is a recent rising scientific interest on the structural and electronic properties of chalchogen elements (S,Se) on Si(100)2x1 surfaces. Theoretical calculations suggest that chalchogen adsorbates change the structure of the Si(100)2x1 surfaces [6,7]. According to our knowledge, this does not agree with the up to-date relevant experimental results. It is well-known that the clean Si(100) surface shows a strong (2x1) reconstruction in the LEED pattern. It has been recently accepted by most researchers that dimers are the main building blocks of the reconstructed surface of Si(100) [6-14]. The restoration of reconstructed semiconductor surfaces to their original bulk-terminated surface has been achieved, lately, by different adsorbates other than S on Si(100) [15-18]. Adsorption of S on clean Ge(100)2x1 changed the (2x1) structure to (1x1). The system S/Ge(1x1) was regarded as an ideal terminated surface[19]. The same authors[20] have, experimentally, investigated the behavior of S on Si(100). They have not observed an ordered S adlayer. Moriarty et al. reported, recently, that room temperature adsorption of sulfur resulted in the formation of an overlayer with the underlying Si(100) retaining the 2x1 reconstruction [21]. They also reported that annealing of the S/Si(100)2x1 surface to 325°C leads to the desorption of the sulfur overlayer and the appearance of coexisting c(4x4) and (2x1) surface reconstruction. In contrast to this report, theoretical studies by Kaxiras [7], and later by Kruger and Pollman [6], suggested that adsorption of group VI elements (S or Se) on Si(100)2x1 can lead to restoration of the ideal bulk-terminated geometry on the semiconductor surfaces. From the above discussion it is apparently clear that additional effort on the study of S and Se on Si(100)2x1 is necessary.

EXPERIMENT

The experiment was performed in an ultra-high vacuum system (UHV) using an Auger electron spectrometer (AES) , a quadrupole mass spectrometer for TDS measurements, a low energy electron diffraction (LEED) system, and a Kelvin probe for work function (WF) measurements. Elemental sulfur was evaporated by thermal dissociation of MoS_2 single crystal flakes mounted on a tungsten filament. The Si(100) substrate was cleaned by Ar+ bombardment at E = 1 keV for 40 min with an ion current of 10 μA. After bombardment the sample was heated to 1000°C by passing current through a 0.05 mm Ta strip, uniformly pressed between the sample and a Ta foil case. The surface atomic density of 1 monolayer of S on Si(100) is considered equal to that of the outermost layer of Si, N_{Si} = 6.8x10^{14} atoms·cm^{-2}.

RESULTS

Fig. 1 shows the Auger peak to peak heights (Ap-pH) of the S(151 eV) versus the number of S doses deposited on clean Si(100)2x1 surfaces at room temperature and the subsequent heating temperatures of the Si substrate for 2 minutes. These measurements are shown in correlation with the observed LEED patterns which will be discussed later in this section. As seen in this figure, the Auger peak to peak height of S(151 eV), initially increases linearly with an increasing number of S doses. Near the ninth dose the curve forms a break (slope change of the S Auger peak height vs S dose curve). The S Auger peak height is increasing up to the eighteenth dose of our measurements where it forms a second break. Above the 18th dose the S(151 eV) peak height starts to level off. With the subsequent heating the S peak height remains nearly constant up to 400°C. Above this temperature the S peak height decreases drastically, indicating removal of S from the surface, which is completed at about 650°C. During the S deposition the energy of the Si Auger peak is shifted linearly with S doses to lower energy by 1.5 eV at the 18th dose (not shown here).This is an Auger chemical shift which may be attributed to a strong binding , probably covalent, between S and Si.

Fig. 2 shows the work function change ($\Delta\Phi$) versus S doses on clean Si(100)2x1 surfaces at room temperature and the subsequent heating temperatures of the Si substrate for two minutes. During the S deposition at room temperature, the work function increases initially linearly with increasing S coverage. Above the fourth S dose the work function curve deviates from linearity and its slope becomes smaller. Near the ninth dose, the work function reaches its maximum value, and subsequently starts to decrease as the number of sulfur doses increases. Above the thirteenth dose the decrease of the work function is very small, despite that the Auger peak height of S(151 eV) continues to increase. We should emphasize that during heating the work function decreases while the S Auger peak height remain nearly unchanged up to 300°C. Most likely, heating provides the activation energy for further diffusion of S into the bulk of the Si substrate causing the work function decrease. Above 400°C the work function increases while the Auger peak of S decreases drastically, indicating a drastic desorption of S from the surface. At about 550°C, the second S layer is removed completely and the work function increases to its maximum value. Above 550°C, as the S coverage approaches the 0.5 ML, the surface changes back to the reconstructed (2x1). Near 650°C the S is completely desorbed from the Si substrate.

The LEED observations show that the clean Si(100)2x1 surface gives a good intense (2x1) LEED pattern. Above the fourth dose of S deposition on this surface, the half-order spots become diffuse and the pattern changes to a (1x1) with its maximum intensity near the ninth dose. Further S deposition increases the background, however, the (1x1) structure remains. It appears that
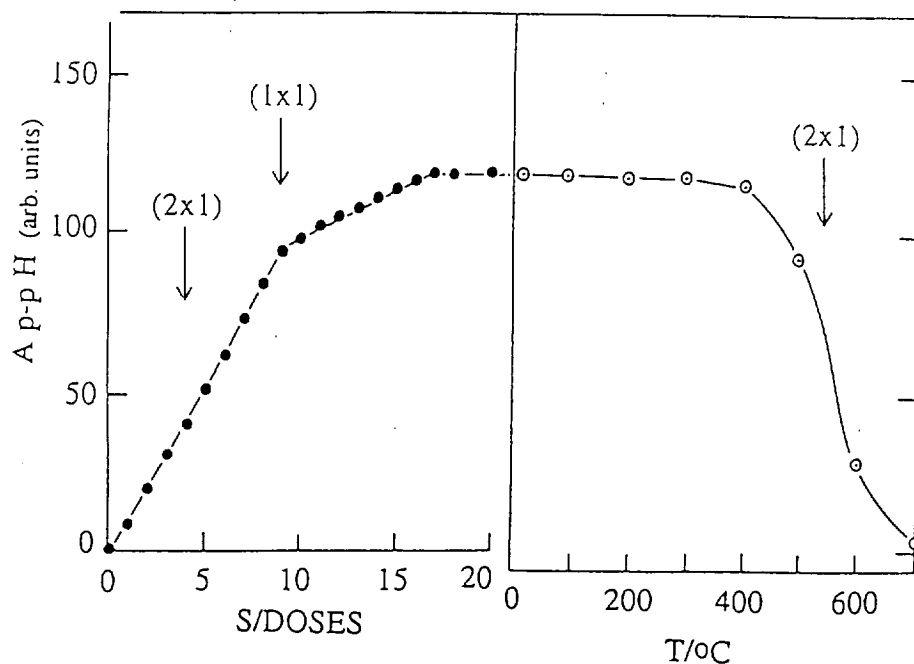
Figure 1. Auger peak to peak heights (Ap-pH) of the S(151 eV) versus the S doses on clean Si(100)2x1 surfaces at room temperature and subsequent heating temperatures of the Si substrate for 2 minutes.
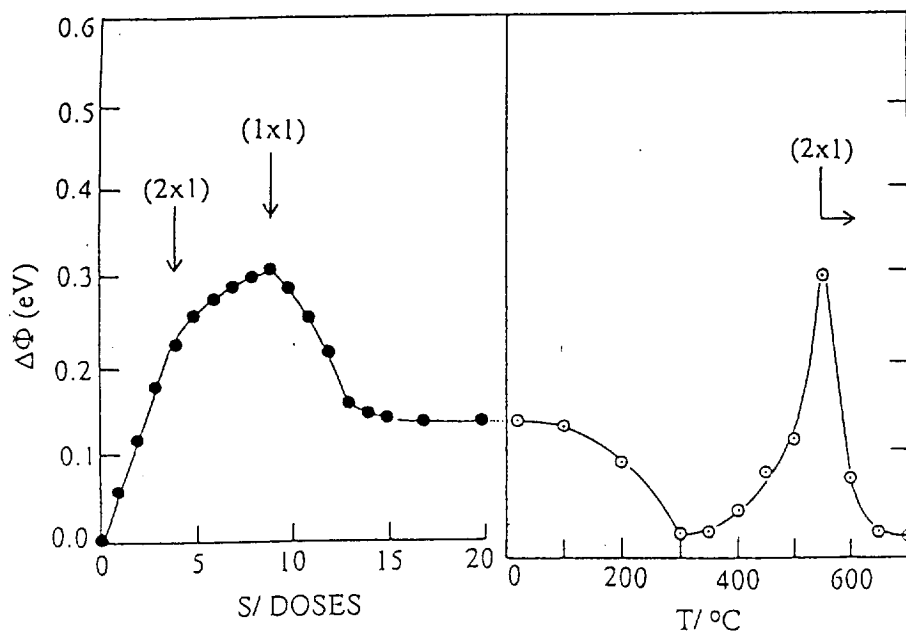

Figure 2   Work function change ($\Delta\Phi$) versus the S doses on clean Si(100)2x1 surfaces at room temperature and subsequent heating temperatures of the Si substrate for two minutes.

above the 4th dose of S the Si(1x1)2x1 reconstructed surface changes to a S(100)1x1. We believe that structural tendencies of the S adsorbate accommodates the changes on the Si substrate. Fig. 3 shows a side view structural model of (a) a reconstructed Si(100)2x1 surface (b) a (2x1) structure of S (0.5 ML) on Si(100)2x1 (c) a (1x1) structure of S (1.0 ML) on Si(100)1x1 (d) a top (1x1) and a diffused (1x1) underlayer of S (~2.0 ML) on Si(100)1x1. (P stands for the surface dipole moment). We propose in this figure that, S on Si(100)2x1 forms also a (2x1) structure, initially. The maximum intensity of the (2x1) pattern, near the 4th dose, should correspond to 0.5 ML of S coverage. Above the 4th dose, both the Si substrate and the S adsorbate change to a (1x1) structure. The completion of the (1x1), near the 9th dose, corresponds to 1.0 ML of S, and coincides with the first break of the Auger curve and the maximum increase of the work function value (Figs 1 and 2). Above the 9th dose ,the (1x1) is retained. Despite that the Auger curve remains linear up to 9th S dose, the work function curve deviates from linearity at the 4th dose. This may be attributed to different S sites before and after the 4th dose. Assuming that the bonding of S on Si is covalent up to 2 ML, the polarization of the electronic charge of the deposited S atoms remains unchanged with increasing coverage. Therefore, any change in dipole moment should be attributed to the dipole length change. Consequently, the S atoms on the dimers of the Si(100)2x1 surface may have greater dipole moment P than on sites on the Si(1x1) surfaces (Fig. 3). In the latter case, the distance between the neighboring Si atoms of the top layer is greater than that between those of the dimers. Therefore, the S adatoms should be deeper in their sites between the Si atoms of the (1x1) surface structure, with a smaller dipole length and, therefore, smaller dipole length and work function. . The fact that, above 1.0 ML (9th dose), the slope change of the Auger curve is rather drastic (Fig. 1), as compared to cases of layer by layer growth [22], and the work function value decreases may indicate that above 1.0 ML the sulfur is submerged into the Si bulk near the surface. The dipole moment of the submerged S atoms compensates that of the S overlayer with a consequent lowering in work function (Fig. 2). Kaxiras, in his calculations [7], considered different structures consisting of embedding and mixing of the group-VI adatoms with Si substrate atoms. This is in agreement with our measurements which indicate an imbedding of the second S layer into the Si bulk.
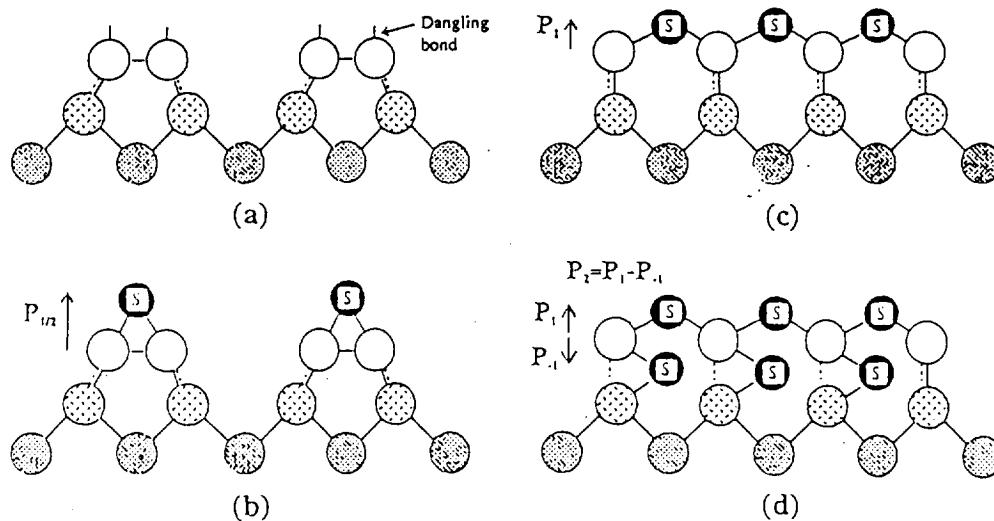

Figure 3   Side view of (a) a reconstructed Si(100)2x1 surface (b) a (2x1) structure of S (0.5 ML) on Si(100)2x1 (c) a (1x1) structure of S (1.0 ML) on Si(100)1x1 (d) a top (1x1) and a diffused (1x1) underlayder of S (~2.0 ML) on Si(100)1x1. (P is dipole moment).

The same UHV system has been used previously with the same S-source, and about the same flax of S on Ni(100) [22]. The LEED observations showed the formation of a c(2x2) pattern close to the 12th dose of S on Ni(100). The density of the S overlayer, which produces the c(2x2) on Ni(100), is $8x10^{14}$ atoms·cm^{-2} at 12 doses. At 9 doses this density should be about $6x10^{14}$ atoms·cm^{-2}. This is very close to $6.8x10^{14}$ atoms.cm^{-2}, which is the density of 1 ML of S on Si(100). Therefore, at the completion of the (1x1) structure on Si(100), the coverage of S at 9 doses is indeed about 1 ML. It has been proposed that the initial sticking coefficient of S on clean Ni(100) is close to unity [23]. This implies that the initial sticking coefficient of S on Si(100)2x1 is also one. The linearity of the Auger curve up to 1 ML (Fig. 1) indicates that the sticking coefficient of S on Si(100) surface remains one, at least, up to 1 ML. The slope of the Auger curve, however, is also constant between the first and the second break, which occurs in about the same time of the completion the first monolayer. This may further imply that the sticking coefficient of S is nearly constant up to the 18th dose where the second layer of S is completed.

CONCLUSIONS

The adsorption of S at room temperature causes the gradual change of the reconstructed Si(100)2x1 to its original bulk-terminated Si(100)1x1 surface. The S adsorbate accommodates the substrate' structural changes. Sulfur, at 0.5 ML, forms a (2x1) on the Si(100)2x1 surface and subsequently, at 1.0 ML, a (1x1) on the Si(100)1x1. Above 1 ML, sulfur is imbedded into the Si bulk near the surface. The sticking coefficient of S on Si(100) surface is constant up to 2 ML. Deposition of S at RT up to 1 ML increases the work function of the surface by about $.3\pm0.05$ eV. Above 1 ML, as the S is diffused into the Si bulk, the work function decreases.

ACKNOWLEDGMENTS

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Adsorption of elemental S on Si(100)2x1: Surface Restoration

Aris Papageorgopoulos and Adero Comer

Department of Physics and Center for High Performance Polymers and Ceramics

Clark Atlanta University, Atlanta, GA 30314, USA

M. Kamaratos and C. A. Papageorgopoulos

Department of Physics, University of Ioannina, P.O. Box 1186,

GR - 451 1 0 Ioannina, Greece

ABSTRACT

Adsorption of elemental S at RT causes the transition of the reconstructed Si(100)2x1 surface to its original bulk-terminated Si(100)1x1. The S adsorbate forms initially a (2x1) structure at 0.5 MLs on the Si(100)2x1 surface, a (1x1) at 1 ML on the Si(100)1x1, and above 1 ML sulfur is imbedded into the Si substrate. The sticking coefficient of S is constant and equal to unity for the first 2 MLs. Deposition of S at RT up to 1 ML increases the work function by 0.3 ± 0.05 eV. The S adsorbate is strongly bound to the Si substrate in a molecular Si-S form. The Si-S bond energy is greater than that of Si-Si, which may be the driving force of the Si(100)2x1 --> Si(100)1x1 transition.

I

I. INTRODUCTION

The passivation of semiconductor surfaces is an area of intrinsic scientific interest and of great technological importance. Silicon and other semiconductors, such as GaAs and InP, are well-known for their potentially wide use in high-speed electronics and long-wavelength optical circuits (optoelectronics)[1,2]. They have also demonstrated great value, mainly in space technology, as solar cells (photovoltaics)[3]. Their efficiency, however, is reduced by electron[4], X-ray[5] and gamma[6] radiation damage. Nonradiative recombination of charge carriers[1] is another such cause. Moreover, interactions with surroundings such as oxidation may cause a depletion, and generally a change of the surface composition. To prevent damage in the surfaces involved without reducing their efficiency the above semiconductors are passivated. This is done by depositing protective films (dielectric window layers), such as chalcogenides: sulfur, gallium sulfide and indium sulfide[7-10]. Most of the studies concerning surface passivation of semiconductors were carried out with the use of chemical vapor deposition techniques under atmospheric pressure. The analysis of the deposited layers with the former techniques has been obtained ex-situ after the completion of films a few hundred nm's thick.

The in-situ analysis of the initial stages of the interface formation in ultra-high vacuum (UHV) is necessary for the understanding and subsequent improvement of the deposition process. The interface region between the adsorbate and the substrate is that which primarily controls the growth of the films. The understanding of the film growth, therefore, requires deposition methods that allow control of the building process of the structure at the atomic level[11]. A beginning with elemental S deposition on Si(100)2x1 in UHV would be appropriate. The knowledge of the behavior of S alone on Si and other semiconductors is very important because: (a) of the interest which has arisen with respect to the possibility of pretreating the surfaces of the semiconductors with S to protect and stabilize these surfaces against degradation resulting in improved subsequent

processing[12,13], and (b) it will help to obtain a better understanding of the binding structure and electronic properties of the growth of chalchogenide protective films such as GaS and InS.

Besides the importance in applications, there is a recent rising scientific interest on the structural and electronic properties of chalcogen elements (S,Se) on Si(100)2x1 surfaces. Theoretical calculations suggest that adsorbates change the structure of the Si(100)2x1 surfaces[14,15]. According to our knowledge, this does not agree with the up todate relevant experimental results. More specifically, the Si(100) surface is easily reconstructed with a small amount of heating. The surface has a structure different from that of the bulk, and the reconstruction of the clean surface occurs in order to reduce the number of broken dangling bonds[14]. In other words, the reconstruction of the surface drives to minimize the high energy of broken covalent bonds, which would exist on an ideal bulkterminated plane[15]. The clean Si(100) deal bulk terminated plane[15]. The clean Si(100) surface shows a strong (2x1) reconstruction in the LEED pattern, observed for the first time by Schlier and Farnsworth in 1959[16]. Several models for the (2x1) reconstruction have been proposed[17]. It has been, recently, accepted by most researchers that dimers are the main building blocks of the reconstructed surface of Si(100). The question, however, of whether the dimers are symmetric or buckled remains unclear, as reported by Chadi[18]. Today, new evidence of asymmetric (buckled) dimers is supported by most of the experimental[19-23] and theoretical[14,15] investigators who have worked on this problem. Kruger and Pollman[14] calculated that buckled dimers are energetically favored over symmetric ones by 0.14 eV per dimer[14]. The restoration of reconstructed semiconductor surfaces to their original bulk-terminated surface has been achieved, lately, by different adsorbates. Specifically, ideal (1x1) terminations of (111) surfaces were reported for As on Ge(111)[24] and Si(111)[25,26] and for Cl on Ge(111)[27]. Adsorption of S on clean Ge(100)2x1 changed the (2x1) structure to (1x1). The system S/Ge(100)1x1 was regarded as an ideally terminated surface[28]. The same authors[10] have experimentally investigated the

behavior of S on Si(100). They have not observed an ordered S adlayer. Moriarty et al.[30] reported, recently, that room temperature adsorption of sulfur resulted in the formation of an overlayer with the underlying Si(100) retaining the (2x1) reconstruction. They also mentioned that annealing of the S/Si(100)2x1 surface to 325 ΓC leads to the desorption of the sulfur overlayer and the appearance of coexisting C(4x4) and (2x1) surface reconstruction. In contrast to this report, theoretical studies performed by Kaxiras[15], and later by Kruger and Pollman[14], suggested that adsorption of group VI elements (S or Se) on Si(100)2x1 can lead to the restoration of the ideal bulk-terminated geometry on the semiconductor surfaces. From the above discussion it is apparently clear that additional effort on the study of S and Se on Si(100)2x1 is necessary.

Most of the sulfur adsorption studies, up to now have taken place with the exposure of the substrates to H_2S gas. To remove the H_2 from the surface the substrates were heated to temperatures equal or greater than 200 °C. Hydrogen, however, cannot be removed selectively. These mixed systems do not show any well defined long range order[28]. For a detailed understanding of the adsorption kinetics of S on Si surfaces at room and lower temperatures, it is important to deposit elemental sulfur.

In this work we evaporate elemental sulfur on Si(100)2X1 surfaces. We study the sample using Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Thermal Desorption Spectroscopy (TDS),and Work Function (WF) measurements. The data suggest that the presence of sulfur on the surface causes a phase transition of the substrate. Preliminary results have been reported in ECOSS and MRS 1995 Fall meetings.

II.   EXPERIMENTAL

The experiments were performed in an ultra-high vacuum chamber ($p<10^{-10}$ Torr), equipped with a cylindrical mirror analyzer (CMA) for AES measurements, a quadrupole mass spectrometer (QMS) for TDS measurements, a LEED system,

and a Kelvin probe for WF measurements.

Elemental sulfur was evaporated by thermal dissociation of MoS_2 single crystal flakes mounted on a tungsten filament. During dissociation of MoS_2 the Mo remained on the tungsten filament, while S was evaporated. The Si(100) substrate was cleaned by Ar^+ bombardment at E=1 keV for 40 min with an ion current of 10 mA. After bombardment the sample was heated to 1000 °C by passing current through a 0.05 mm Ta strip, uniformly pressed between the sample and a Ta foil case. The temperature of the sample was measured by a Cr-AI thermocouple. The Si specimen was considered sufficiently clean when the Auger peak height ratios C(272 eV)/Si(92 eV) and O(512 eV)/Si(92 eV) were below 1%. The estimation of the S coverages on Si(100) surfaces were based on a correlation of LEED, AES and TDS measurements, and the comparison with the measurements of S on the Ni(100) surface which took place in the same system under the same deposition conditions[31]. The surface atomic density of 1 monolayer of S on Si(100) is considered equal to that of the outermost layer of Si, $N_{Si}=6.8 \times 10^{14}$ atoms·cm^{-2}.

III.   RESULTS

Auger and Work Function   measurements

Figure 1 shows the Auger peak to peak heights (Ap-pH) of the S(151 eV) and the work function ($\Delta\Phi$) change as a function of the number of doses of S deposited on clean Si(100)2x1 surfaces at room temperature. These measurements are shown in correlation with the observed LEED patterns which will be discussed later in the next section. As seen in this figure, the Auger peak to peak height of S(151 eV), initially increases linearly with an increasing number of S doses. Near the ninth dose, the curve forms a break (slope change of the S Auger peak height vs S dose curve). Also above the 9th dose the S Auger peak height is increasing linearly up to the eighteenth dose of our measurements where it forms a second break. Above the 18th dose the S(151 eV) peak height starts to level off. This Auger peak

height vs S doses curve is characteristic of a layer by layer growth. During the S deposition on the clean Si(100)2x1 surface at room temperature, the work function initially increases linearly with increasing S coverage. Above the fourth S dose the work function curve deviates from linearity and its slope becomes smaller. Near the ninth dose, the work function reaches its maximum value, and subsequently starts to decrease as the number of sulfur doses increases. Above the thirteenth dose the decrease of the work function is very small, despite that the Auger peak height of S(15 1 eV) continues to increase. The maximum observed value of the WF increase was about 0.3 eV. The above WF measurements were repeated three times, and the maximum WF value varied by +0.05 eV. Fig. 2 shows the energy shift of the integrated Auger Si(92 eV) peak during S deposition on clean Si(100)2x1. The insert shows the Si(92 eV) energy shift versus S doses. According to the insert, this shift increases linearly with increasing S doses to its final value of 1.5 eV at the completion of the second layer of S. During heating and as the S is removed from the surface the shift decreases and the energy of the Si peak goes back to that of the clean Si surface. This is an Auger chemical shift which may be attributed to a strong S-Si interaction. Most likely, the S adatoms form a compound with the Si substrate. The fact that the shift increases linearly may indicate that the nature of binding is the same up to the completion of the second layer, in agreement with the following TDS measurements.

TDS measurements

Thermal desorption spectra from S-covered Si(100) surfaces have shown hardly observable peaks of S_2 (amu 64). Sulfur was mainly desorbed as a SiS compound. Fig. 3 shows a series of SiS (amu 60) of thermal desorption spectra for different amounts of Si deposited on S(100) surfaces. The heating rate of desorption was constant, b =20 K/s, for all spectra. There is only a single peak with its maximum value near 585 °K, the very small peaks of S_2, not shown here, appear

at the same temperature and probably are due to a partial dissociation of the SiS molecule. This finding does not agree with Moriarty et al.[30], who reported that the annealing of the S covered Si(100)2x1 surface to 325 °C leads to the desorption of the sulfur overlayer. The latter disagreement will be also discussed in correlation with other findings in the discussion. The fact that the TD peaks of SiS remain relatively sharp at the same temperature with increasing S coverage indicates that the nature of Si-S binding remains the same up to the completion of the S coverage corresponding to the completion of 2 MLs, in agreement with the chemical shift measurements.

Fig.4 shows the areas under the TD peaks of SiS (Fig. 3) versus the S doses on Si(100) surfaces. Note that the S doses in the TDS were 15% greater than those in the previous(AES and WF) measurements, and the completion of 2 ML's of S in Fig. 4 occurs at the 1 5th dose. It is obvious, from this figure, that the TDS areas increase linearly with increasing number of S doses, with a break (slope change of the SiS TDS areas versus S doses curve) occurring near the 15th dose of S, this is where we believe that the completion of 2 ML's of sulfur takes place. It is known that the slope of the areas under the TDS versus doses of a deposited adsorbate on a substrate is proportional to the sticking coefficient of the adsorbate. This, in correlation with Fig. 4, implies that the sticking coefficient of S on Si(100) surfaces remains constant up to 2 MLs and subsequently becomes substantially smaller.

LEED measurements

The LEED observations show that the clean Si(100)2x1 surface gives a good intense (2x1) LEED pattern. Above the fourth dose of S deposition on this surface, the half-order spots become diffused and the pattern changes to a (1x1) with its maximum intensity near the ninth dose. Further S deposition increases the background, however, the (1x1) structure remains. It appears that above the 4th dose of S the Si(100)2x1 reconstructed surface begins to change to a S(100)1x1. We

believe that S adsorption on Si(100)2x1 forms also a (2x1) structure, initially. The (2x1) pattern, near the 4th dose, should correspond to 0.5 ML of S coverage. Above the 4th dose, both the Si substrate and the S adsorbate change to a (1x1) structure. The completion of the (1x1), near the the dose, corresponds to 1.0 ML of S, and coincides with the first break of the Auger curve and the maximum increase of the work function value (Fig. 1). Above the 9th S dose, the (1x1) is retained.

The same UHV system has been used previously with the same S-source, and about the same flux of S on Ni(100)[31] The LEED observations showed the formation of a c(2x2) pattern close to the 12th dose of S on Ni(100). The density of the S overlayer, which produces the c(2x2) on Ni(100), is 8×10^{14} atoms.cm^{-2} at 12 doses. At 9 doses this density should be about 6×10^{14} atoms.cm^{-2}. This is very close to 6.8×10^{14} atoms.cm^{-2}, which is the density of 1 ML of S on Si(100). Therefore, at the completion of the (1x1) structure on Si(100), the coverage of S at 9 doses is indeed about 1 ML. It has been proposed that the initial sticking coefficient of S on clean Ni(100) is close to unity[32]. This implies that the initial sticking coefficient of S on Si(100)2x1 is also one. The linearity of the Auger curve up to 1 ML (Fig. 1) indicates that the sticking coefficient of S on Si(100) surface remains one, at least, up to 1 ML. The slope of the Auger curve is also constant for the second monolayer, between the first and the second break, which occurs in about the same time of completion as that of the first monolayer. This may further imply that the sticking coefficient of S is nearly constant during the adsorption of the second S layer, between the 9th and 18th doses. Moreover, the TDS measurements (Fig. 4) indicate clearly that the sticking coefficient remains constant and, therefore, equal to unity up to the completion of 2 MLs of S coverage.

Despite that the Auger curve remains linear and the sticking coefficient remains constant up to 9th S dose, the work function curve deviates from linearity at the 4th dose. This may be attributed to different sites of S atoms on Si before

and after the 4th dose. Both the chemical shift (Fig. 2) and the TDS (Fig. 4). measurements indicate that the nature of binding of S atoms on Si remains the same up to 2 MLs of S, which may imply that the charge transfer (polarization) for each S adatom remains also the same. Therefore, any change to the surface dipole moment should be attributed to the dipole length change. Consequently, the sulfur atoms residing on the dimers of the Si(100)2x1 surface may have greater dipole moment (dipole length) than on sites between Si atoms of the Si(1x1) surface. In the latter case, the distance between the neighboring Si atoms of the top layer is greater than that between those of the dimers of the reconstructed surface. Therefore, the S adatoms should be deeper in their sites between the Si atoms of the (1x1) surface structure, with a smaller dipole length, therefore, smaller dipole moment and consequently a smaller work function than that for S atoms on the dimers. This will be explained in more details in the discussion. The fact that, above 1.0 ML (9th dose), the work function value decreases, while the sticking coefficient and the nature of binding of S on Si remain constant, may indicate that above 1.0 ML the sulfur is submerged into the Si bulk near the surface. Since the WF lowering almost stops before the S coverage completion of 2 MLs means that only part of the second layer is initially diffused into the bulk of Si at room temperature.

Heating of S-covered Si(100)2x1 surfaces

Fig. 5 shows the variation of the Auger peak to peak height (Ap-pH) of S(151 eV) and the work function change ($\Delta\Phi$), in correlation with the LEED patterns, during the heating of the S-covered Si(100)2x1 substrate. The heating was implied in 50 °C increments for two minutes each. We should emphasize that the work function decreases in the early stages of the heating treatment and reaches its minimum value at 300 °C, while the Auger peak height remains nearly unchanged up to 400 °C i.e., at which the S is not yet removed from the surface. Most likely,

heating provides the activation energy for diffusion of more S atoms into the bulk of the Si substrate causing a further work function decrease. Above 400 °C, the work function increases while the Auger peak of S decreases drastically, indicating a drastic desorption of S from the surface. At about 550 °C, the second S layer is removed completely and the work function increases to its maximum value of 1 ML. Above 550 °C the WF decreases again and as the S coverage approaches the 0.5 ML, the surface changes back to the reconstructed (2x1). Near 650 °C the S is completely desorbed from the Si substrate.

IV   DISCUSSION

As we have mentioned previously, the current experimental LEED observations show very clearly that deposition of elemental sulfur on clean Si(100)2x1 surfaces, at room temperature, changes the Si(100)2x1 reconstructed surface to a Si(100)1x1. This phase transition, is reported for the first time. We believe that the S adatoms initially reside on the dimers forming a (2x1) at 0.5 ML and a (1x1) above this coverage. In fig. 6 we propose a surface structural model of sulfur on Si(100) surfaces. Fig. 6a shows a schematic side-view of the top three layers of the clean reconstructed Si(100)2x1 surface with the dangling bonds. The deposited S atoms originally reside on bridge sites. Each S atom is specifically bound through the dangling bonds on the two Si atoms of the dimer (fig. 6b), which is consistent with the fact that S is divalent. The maximum coverage of this state is 0.5 ML at which all the dimer sites are filled, and the S adatoms form a (2x1) structure retaining the reconstruction of the Si substrate. This (2x1) structure of the S overlayer on the Si(100)2x1 surface has been named the hemisulfide state. As the S deposition on the Si substrate continues above 0.5 MLs, the S atoms which reside on available bridge sites between dimers cause the bonds between the Si atoms of the dimers to break, thus providing bonding for the S adatoms. As a result of this process, the Si atoms are gradually displaced, causing the restoration of the reconstructed Si(100)2x1 to a Si(100)1x1 surface. The sulfur adatoms remain

on the bridge sites, and are bound to neighboring Si atoms as it is shown in fig. 6c. Thus, above 0.5 ML, S gradually forms a S(1x1) structure causing the change of the Si substrate to an ideal bulk-terminated plane. This S(1x1) structure on Si(100)1x1 has been named the monosulfide state with a maximum coverage of 1 ML. Above 1 ML, S continues to be adsorbed with the same sticking coefficient up to the coverage of 2 ML. Most of the 2nd monolayer of S is initially diffused into the bulk of Si and later the diffusion decreases and Sremains on the surface. The heating of 300 °C provides activation energy for further diffusion with a simultaneous decrease of the WF. Fig. 6d shows a possible binding of the embedded S atoms which we call disulfide state. Fig. 7 shows a top view of: (a) a clean Si(100)2x1 surface, (b) the hemisulfide on Si(100)2x1, (c) the monosulfide on Si(100)1x1 and (d) the disulfide on Si(100)1x1 .

The break of the bond between the Si atoms of the dimers and the subsequent rearrangement to a (1x1) structure is consistent with a strong Si-S interaction. This strong interaction is suggested by the chemical shift of the Auger Si(92 eV) peak during S deposition (fig. 2) and the TDS measurements (fig. 3). the latter measurements show that the S is desorbed as a SiS molecule, indicating clearly that the Si-S bond energy is greater than that of Si-Si, which may indeed be the dominant cause of the substrate restoration to a Si(100)1x1. The greater S-Si bond energy than that of Si-Si substrate has been reported some time ago[33]. The heating results (fig. 5) indicate that, as soon as part of the S is desorbed from the surface and the coverage is $\leq$ 0.5 ML the reconstructed (2x1) comes back again. Our model of S adsorption on the Si substrate is in agreement with Kaxiras'[15], and later with Kruger and Pollman's[16] theoretical calculations. According to their results adsorption of S or Se causes the surface restoration of the reconstructed Si(100)2x1 substrate to its original bulk terminated surface. Kaxiras, in his report, considered different structures consisting of embedding and mixing of the group-VI adatoms with Si substrate atoms. He emphasizes, however, that the restored surfaces are stable against all of the considered alternative structures. This in

agreement with our measurements which indicate an imbedding of the second S layer into the Si bulk.

Next, we'll try to justify the WF variations in correlation with the corresponding adsorption sites of S on the Si substrate. As it is explained in the section "results", the surface dipole moment changes are mainly due to those of the dipole length which are dictated by site changes of the S on the Si substrate. However, the WF changes are proportional to the dipole moment (eq.1).

From the initial slope of the WF curve (fig.1) the initial dipole moment of S may be calculated by the Hemholtz equation:

$$p_0 = (1/2\pi)(\Delta\Phi/\Delta N)_{N\to 0} = 1/2\pi \ 300 \cdot 10^{-18}(\Delta\Phi/\Delta N)_{N\to 0} \quad \text{Debye} \quad (1)$$

where the sulfur atomic density $N = \Theta_S \cdot 6.8 \cdot 10^{14}$ atoms.cm^{-2}, and Θ_S is the coverage of S in monolayers. The initial dipole moment of S was found to be $p_0 = 0.4$ Db (Debye). If it is considered that in the hemisulfide state the S atoms reside on the dimers as in fig. 6a and 8a, and that $p_0 = qd$ or $q = p_0/d$, where q is the charge of each S adatoms and d= 1.87 A, it is found that q= 0.04e (where e is the charge of an electron). This indicates that the charge of the S overlayer is very small to consider the bonds of S on the Si substrate as ionic. Most likely, the S-Si bond is covalent, in agreement with the chemical shift (fig. 2) and the TDS measurements (fig. 3). After the restoration, the distance between the S overlayer and the topmost layer of the Si substrate decreases and becomes d= 1.09 A (fig. 8b). Considering this dipole length and the finding that q= 0.04e, it is found that $p_0 = qd = 0.2$ Db. Therefore, the value of p_0 is smaller in the monosulfide state than in the hemisulfide. This is consistent with the decrease in slope and deviation from linearity of the WF curve above 0.5 ML of S (4th dose) on Si(100) (fig. 1), when the reconstructed (2x1) Si surface startes to change to its' (1x1).

During the binding of S to the dimers of the Si substrate, we cannot preclude a decrease of the Si substrate WF due to a transition of the asymmetric dimers to

their symmetric arrangement. It has already been mentioned in the introduction the existing view that the dimers of the Si(100) are buckled. This asymmetric deformation increases the dipole moment of the dimers, and the WF is greater than that of the substrate with unbuckled (symmetric) dimers[1,8,34]. The existence of the asymmetric dimers is supported experimentally by ion scattering[19,20] and LEED experiments[21]. Recent STM[22,23] measurements and theoretical calculations[14,15] make the view of asymmetric dimers even stronger. From our measurements it is not clear that the dimers remain asymmetric in the hemisulfide state or that during S deposition the asymmetric dimers change to symmetric. In the latter case, the increase of the work function during S deposition in the hemisulfide state would be compensated to some degree by the WF lowering during the transition of the asymmetric dimers to their symmetric state. The increase of the WF in the hemisulfide state ,however, was very close to 0.25 eV measured (in the same UHV system) for 0.5 ML of S on Ni(100)[31] surface, which may indicate that the increase in WF up to 0.5 ML was due to the adsorption of S alone and not to any structural change of the dimers.

Besides the theoretical support[14,15] on the restoration of the semiconductor surfaces to their original bulk-terminated geometry achieved by S and Se adsorbates, there are also several experimental results mentioned in the introduction. These results, however, refer to As on Ge(111)[24] and on Si(111)[25,26], and to Cl on Ge(111)[27] Weser et al[28] reported that S on Ge(100)2x1 changed the (2x1) structure to (1x1) and that the S/Ge(100)1x1 system was regarded as an ideal terminated surface. The same authors, however, have not observed any S overlayer on the Si(100)2x1 surface[29]. Recently, Moriarty et al[30] reported that room temperature adsorption of S resulted in the formation of an overlayer on Si(100)2x1, retaining the (2x1) reconstruction. They also report that annealing of S covered Si(100)2x1 at 325 ΓC leads to the desorption of the sulfur overlayer. As it is already mentioned, the complete removal of S takes place by heating the substrate to 650 ΓC. The same authors, in continuing their investigation,

discovered coexisting c(4x4) and (2x1) surface reconstructions after the desorption of S at 325 ГС. Our finding that S is desorbed as SiS molecule show that heating causes depletion of Si from the surface. Annealing at relatively low temperatures would cause a partial removal of Si from the surface which could change the reconstruction from (2x1) to a c(4x4). Although our structural models are consistent with the experimental results, we cannot rule out completely the possibility that, from the beginning of deposition, S forms 2D-islands of (1x1). Above a certain coverage, the islands coalesce leading to a uniform (1x1) structure at 1 ML. More work is needed to be done.

V.   CONCLUSION

The adsorption of elemental S at room temperature causes the change of the reconstructed Si(00)2x1 substrate to its original bulk-terminated Si(100)1x1 surface. The S adsorbate forms initially a (2x1) stucture at 0.5 ML on the Si(100)2x1 substrate and subsequently a (1x1) on the Si(100)1x1. Above 1 ML, sulfur is imbedded into the Si bulk near the surface. The sticking coefficient of S on Si(100)2x1 surface is constant and equal to unity for the first 2 MLs. Deposition of S at RT up to 1 ML increases the work function of the surface by about 0.3 ± 0.05 eV. Above 1 ML, as the sulfur is diffused into the Si bulk, the work function decreases. Surface dipole moment estimations based on the work function measurements suggest that the Si-S bond is covalent. The deposition of S causes a chemical shift of the Si(92 eV) peak of 1.5 eV, indicating a strong S-Si interaction. While the TDS measurements show that S is mainly desorbed in the form of SiS compound. This result supports the argument that the Si-S bond energy is greater than that of Si-Si, which may be the driving force of the Si(100)2x1 --> Si(100)1x1 transition.

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FIGURE CAPTION

Figure 1.   Auger peak to peak heights (Ap-pH) of the S(151 eV) and the work function ($\Delta\Phi$) change as function of the number of doses of S deposited on clean Si(100)2x1 surfaces at room temperature

Figure 2.   Energy shift of the integrated Auger Si(92 eV) peak during S deposition on clean Si(100)2x1. The insert shows the Si chemical shift versus S doses.

Figure 3.   Thermal desorption spectra of SiS from S-covered Si(100) surfaces.

Figure 4.   Areas under the thermal desorption peaks of SiS (Fig. 3) and S_2 versus S doses on Si(100) surfaces.

Figure 5.   Variation of the Auger peak to peak height (Ap-pH) of S(151 eV) and the work function change ($\Delta\Phi$) during the heating of the S-covered Si(100)2x1 surfaces.

Figure 6.   Side-view schematics of (a) the top three layers of clean reconstructed Si(100)2x1 surface with the dangling bonds, (b) the S-(2x1) (hemisulfide) structure on the Si(100)2x1 surface, (c) the S-(1x1) (monosulfide) structure on Si(100)1x1 surface, and (d) the diffused second S layer into the bulk of Si(100)1x1.

Figure 7.   Top-view schematics of (a) the top three layers of the clean reconstructed Si(100)2x1 surface, (b) the S-(2x1) structure on the Si(100)2x1 surface (c) the S-(1x1) structure on Si(100)1x1 surface and (d) the diffused second S layer into the bulk of Si(100)1x1.

Figure 8.   Location of the S atoms (a) on the Si(100)2x1 surface, (b) on the Si(100)1x1 surface.
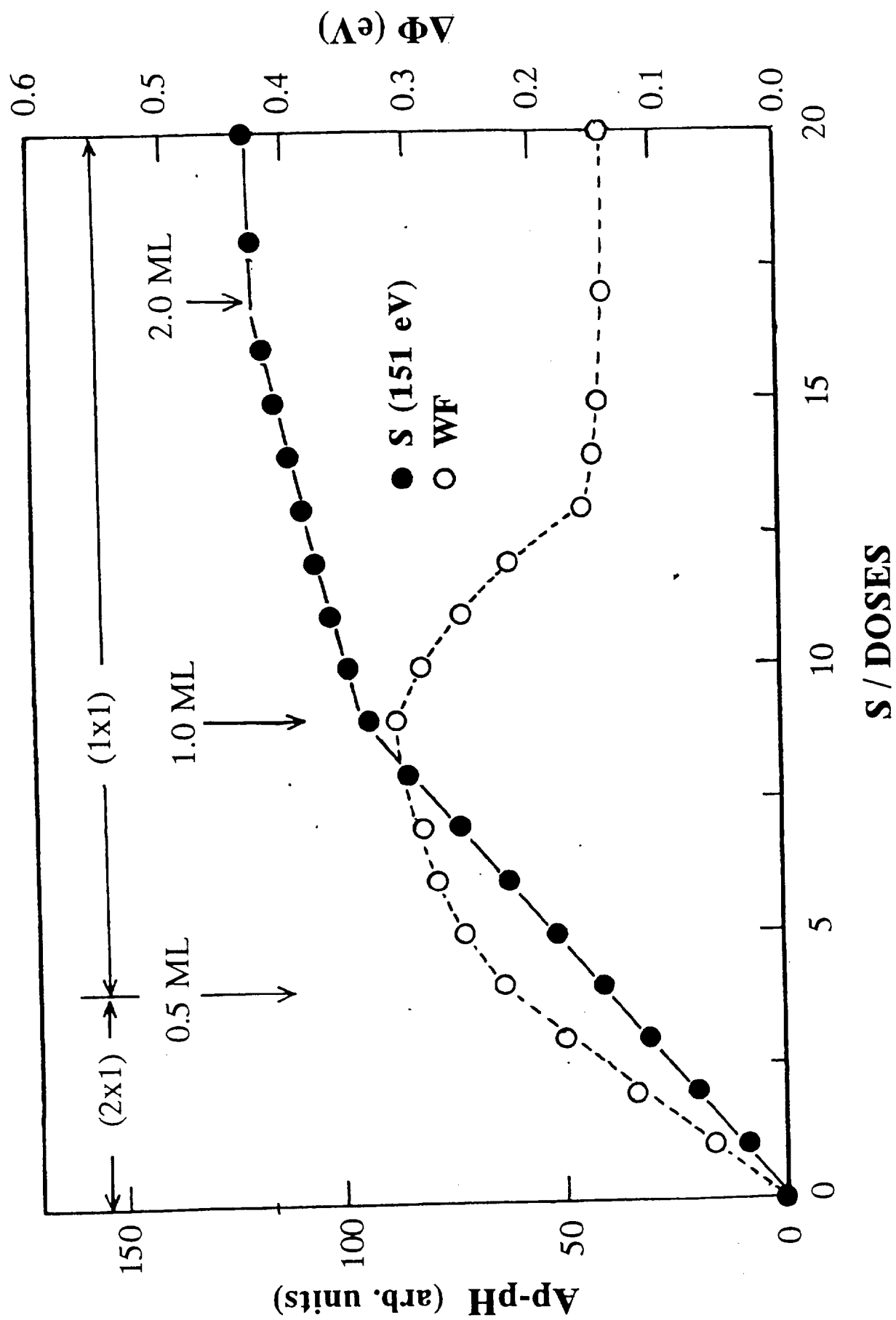
Fig. 4. Work Functions etc. of
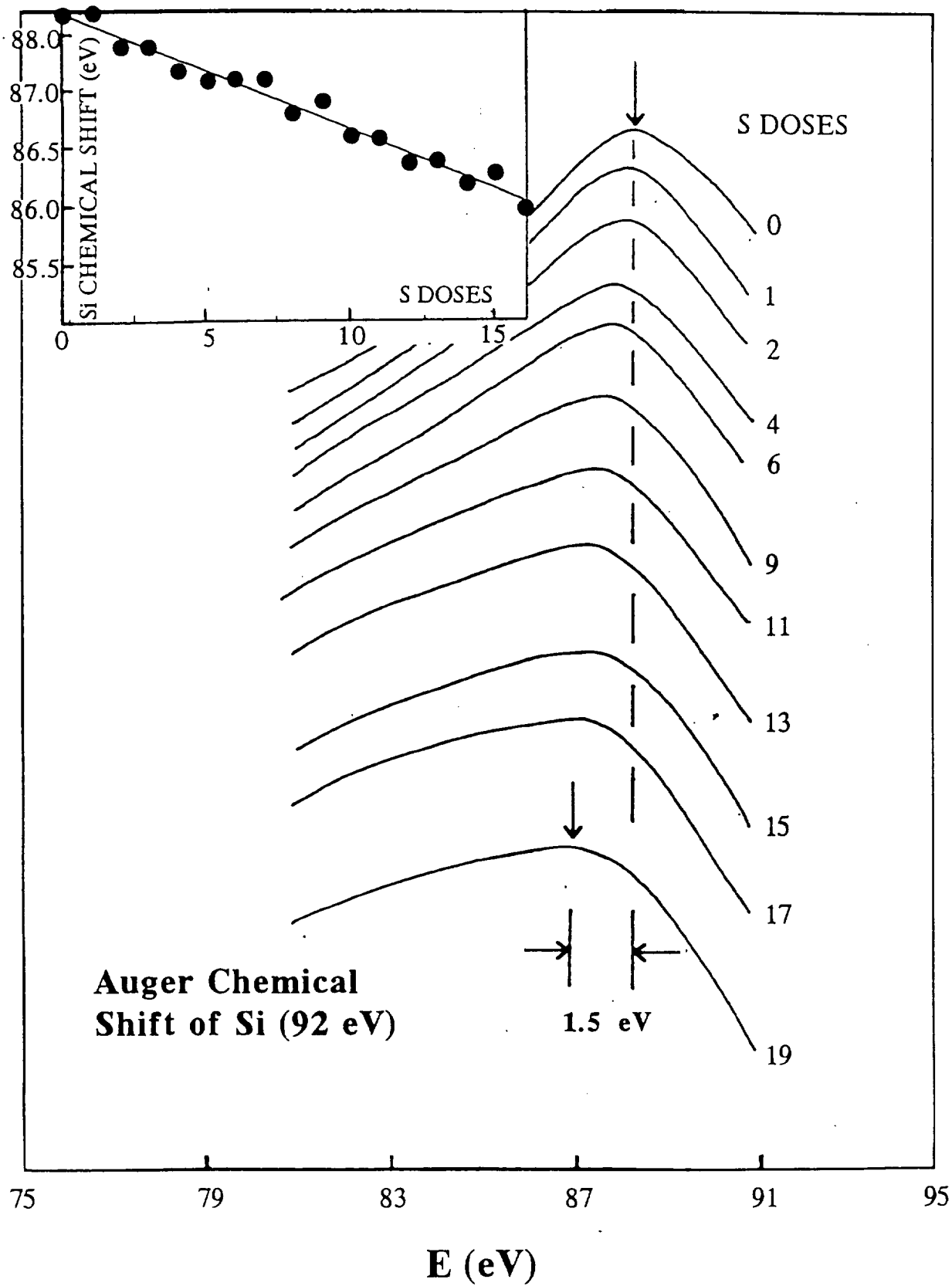
INTENSITY (arb.units)

E (eV)

Si CHEMICAL SHIFT (eV)

S DOSES

88.0
87.0
86.5
86.0
85.5

0   5   10   15

S DOSES

0
1
2
4
6
9
11
13
15
17
19

Auger Chemical Shift of Si (92 eV)

1.5 eV

75   79   83   87   91   95

Fig. 4 Jean Pequerin-Inquerdon et al.

Dangling bond

(a)

(b)

(c)

(d)

Fig. 6

(a)

Second layer
Top layer
Pedestal
[1̄10]
Valley bridge
Third layer
Cave
Bridge

(b)

(c)

(d)

underlayer

1.87 $\overset{0}{A}$

(a)   S/Si (100) 2x1

1.09 $\overset{0}{A}$
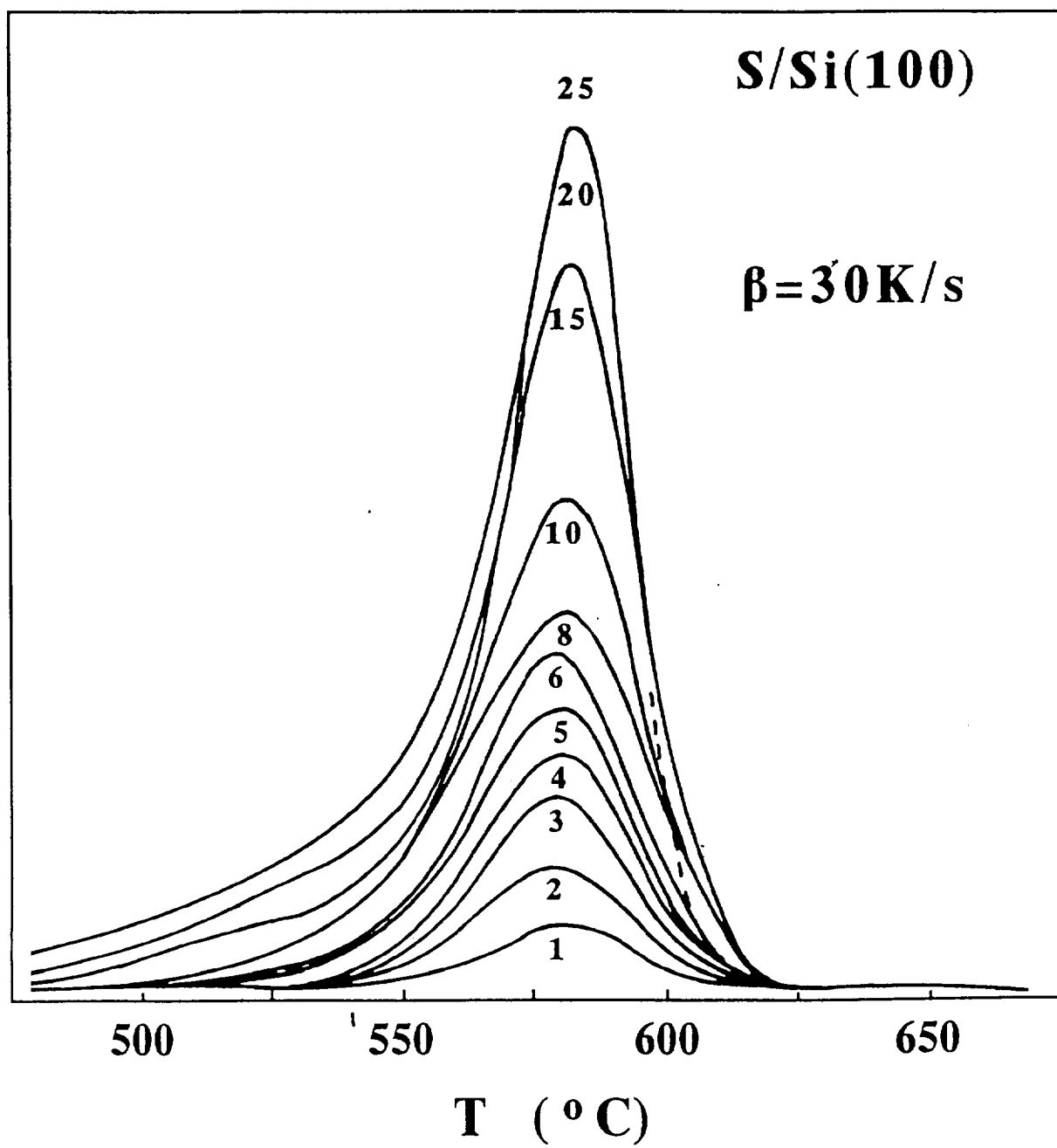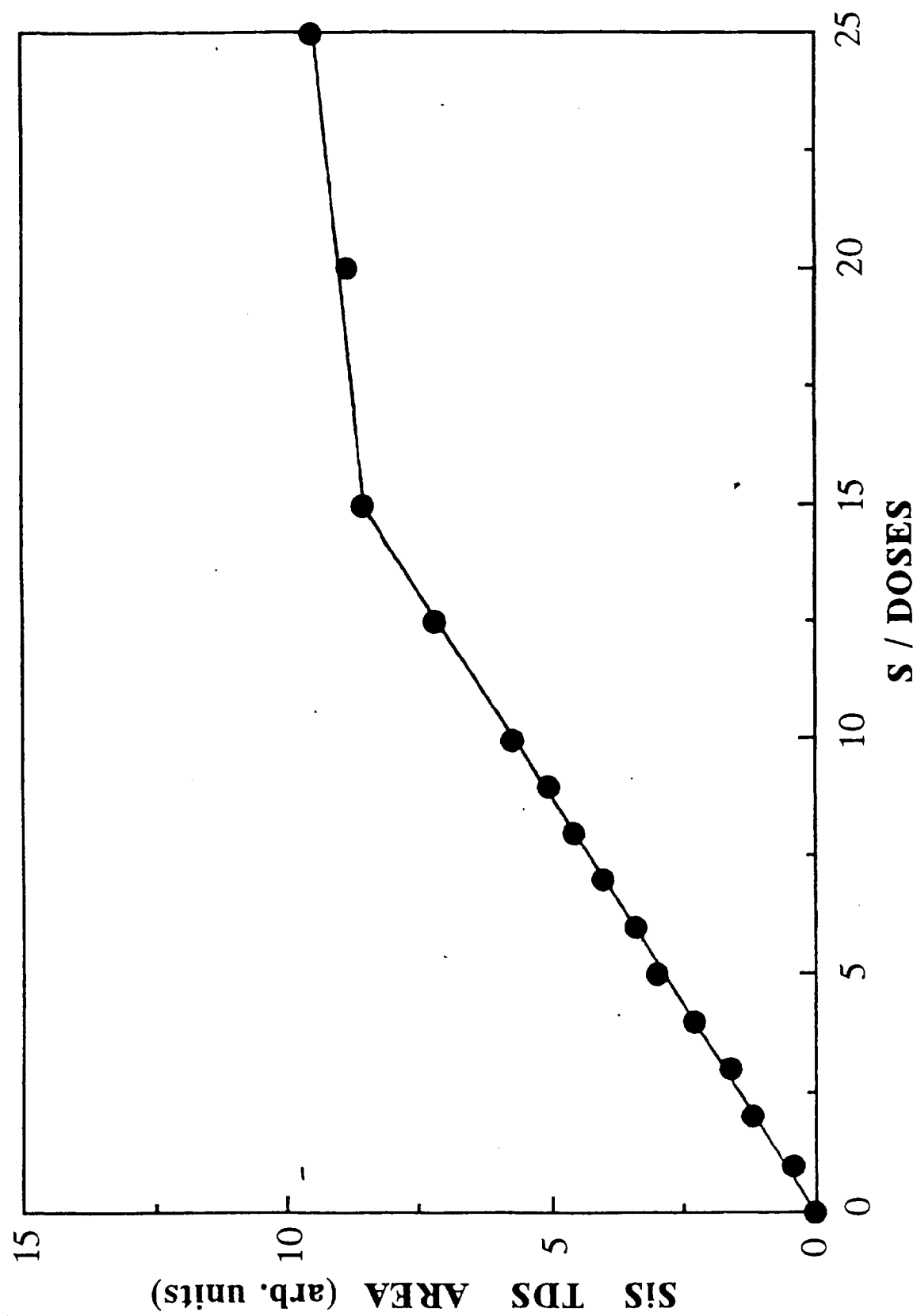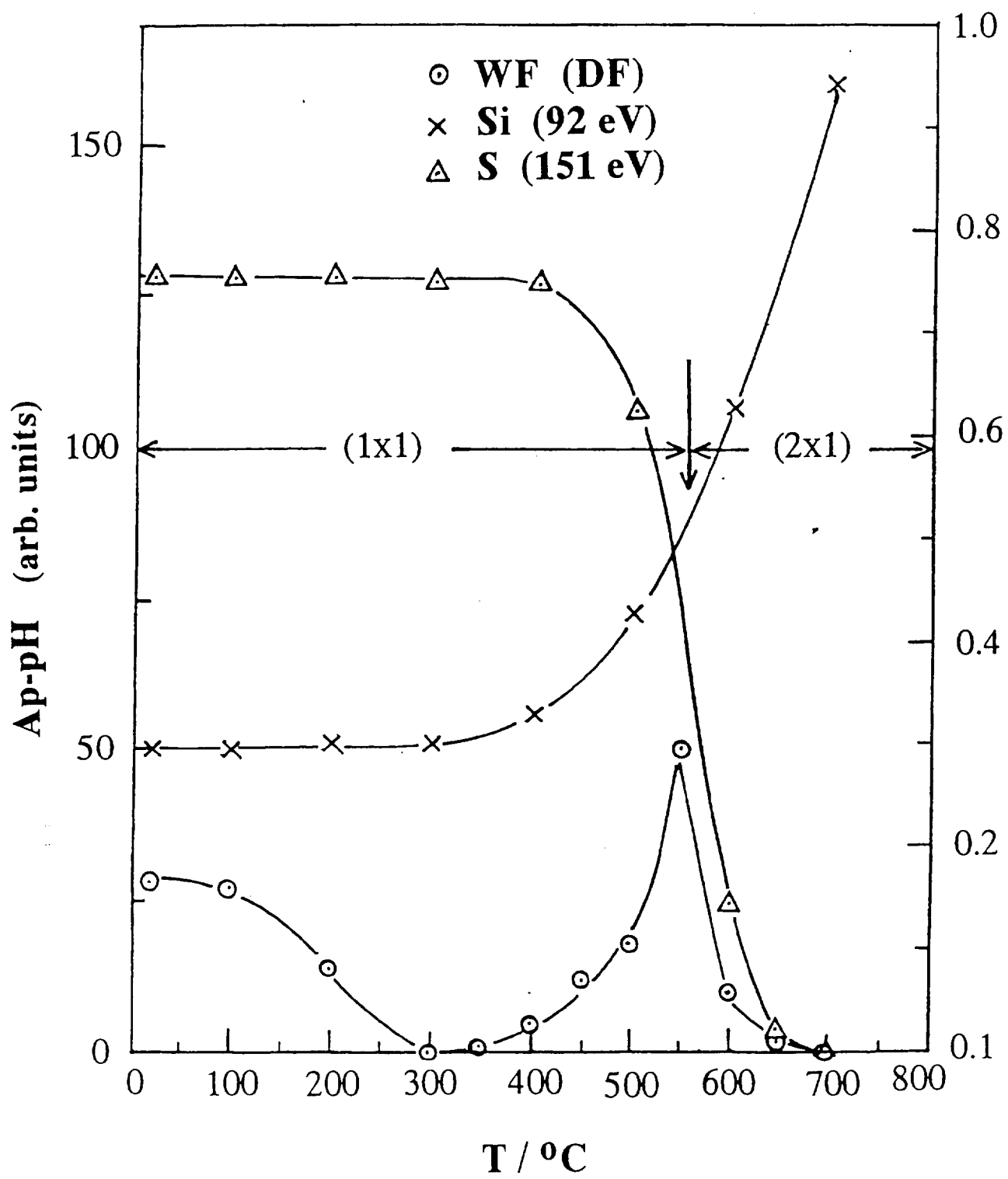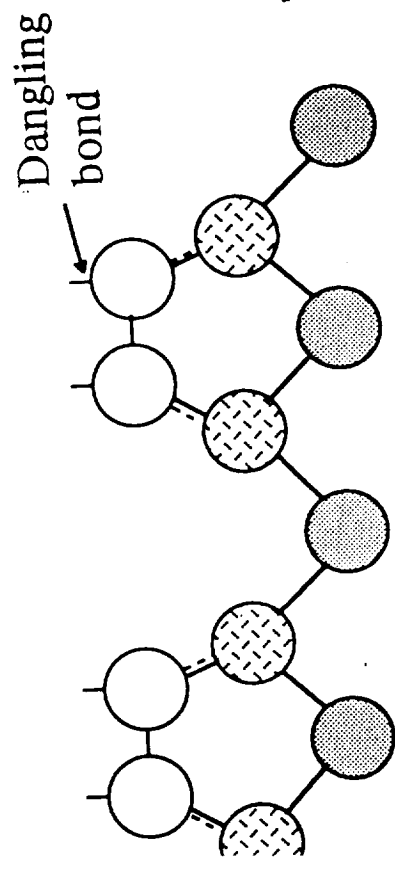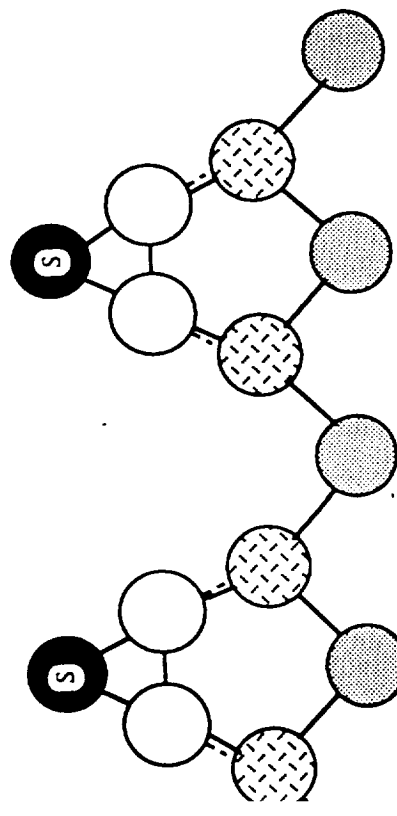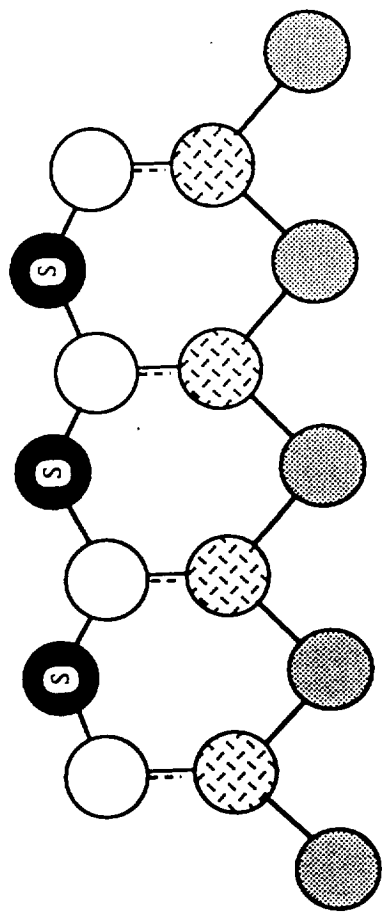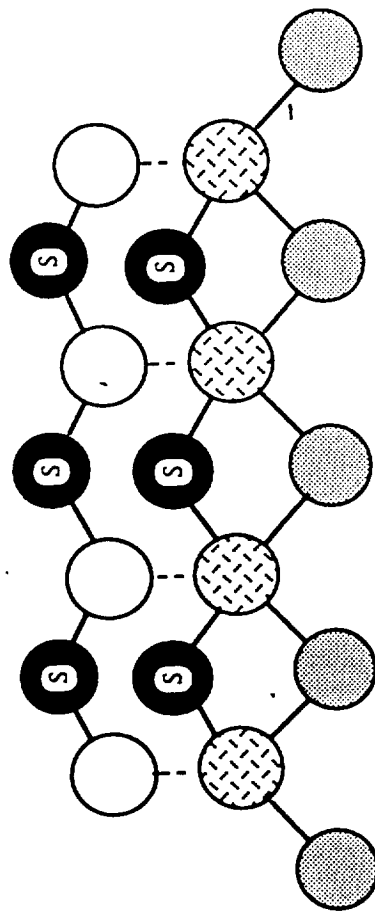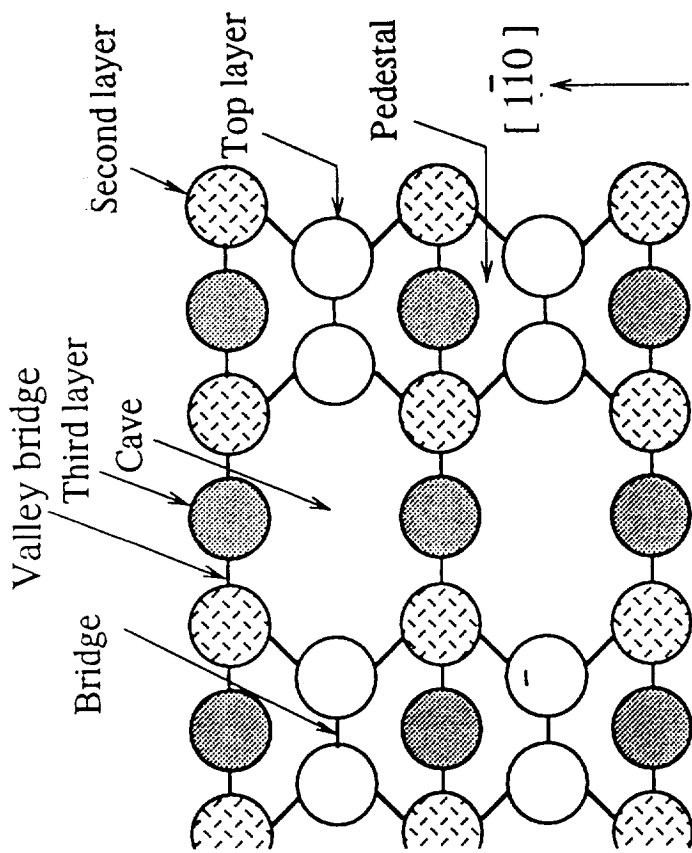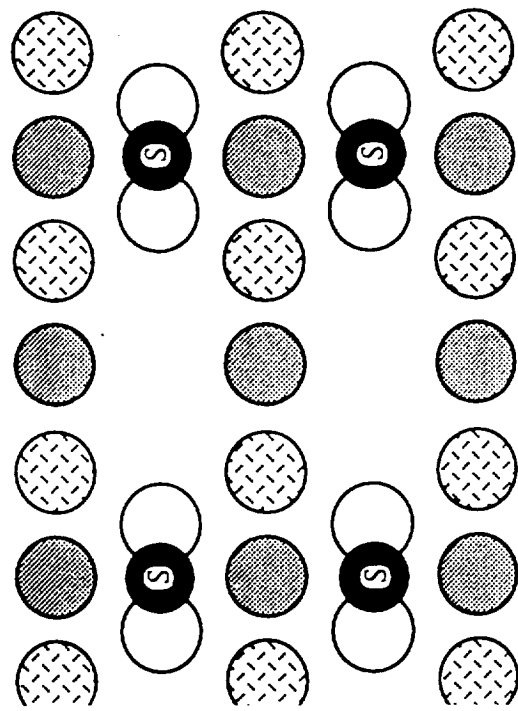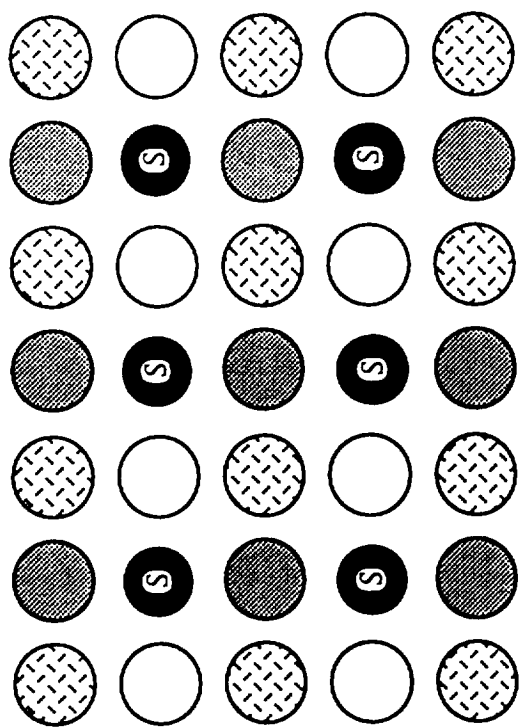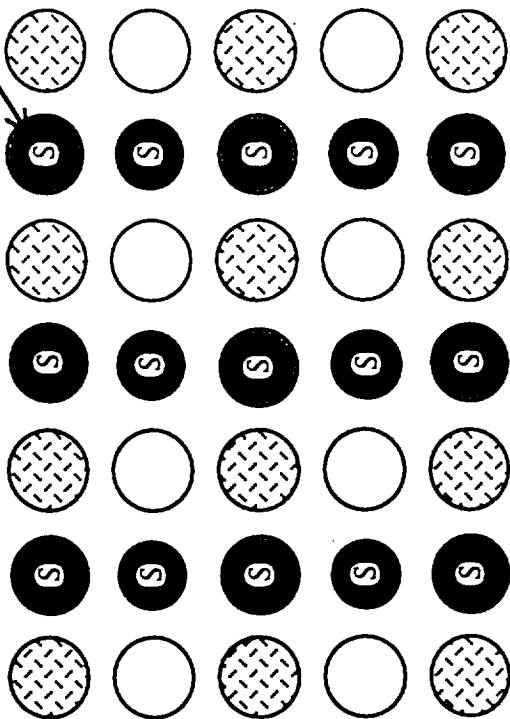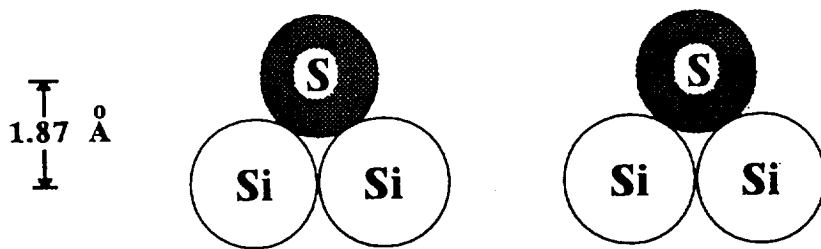
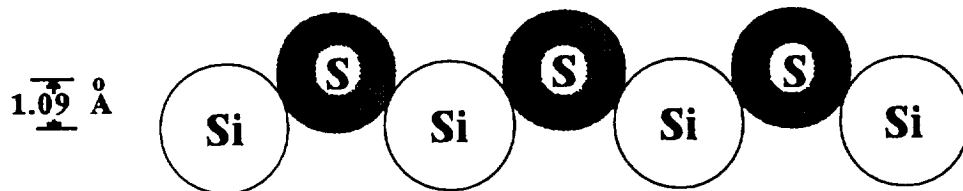**(b)   S/Si (100) 1x1**

Adsorption of Cs on S - covered Si(100) surfaces

Aris Papageorgopoulos, D. C. Papageorgopoulos*

*Department of Physics, Clark Atlanta University.
James P. Brawley Drive at Fair Street S. W., Atlanta, GA 30314,*

Abstract

This paper describes the adsorption of Cs on clean Si(100)2x1, on 0.5 MLs of S- covered Si(100)2x1, and on 1 ML of S-covered Si(100)1x1 surfaces at RT. This is based on our recent report that adsorption of elemental sulfur above 0.5 MLs on clean Si(100)2x1 causes the change of the reconstructed Si(100)2x1 to a Si(100)1x1 surface. The investigation takes place in ultra high vacuum (UHV) system with Auger electron spectroscopy (AES) and work function (WF) measurements. The saturation coverage of Cs on clean Si(100)2x1 surface at RT is 1ML. The presence of predeposited S on the Si(100)2x1 surface increases the binding energy and the maximum amount of Cs that can be deposited on the Si(100) surface at RT. Adsorption of Cs on clean Si(100)2x1 gives the characteristic work function curve of alkali on metals and most semiconductors, i.e. an initial minimum and subsequent increase towards the value of metallic Cs. Preadsorption of S on Si(100)2x1 further lowers the WF during subsequent Cs deposition by about 4 eV to a plateau without the final increase which characteristic of the overlayer's metalization. This is consistent with a covalent bonding of S with the Si substrate. The stable minimum WF value of Cs on the S-covered Si(100)1x1 surfaces might be very interesting for low work function devices (cathods, energy converters).

Keywords: Auger electron spectroscopy; Work function measurements; Silicon; Cesium; Sulfur.

I.   Introduction

The adsorption of alkali on semiconducting substrates is an area of scientific interest and great technological importance. Alkali-semiconductor interfaces are also very important for understanding interfacial metallization and Schottky barrier formation [1]. Special effort has been given to alkali adsorption on Si(100) surfaces. It has been proposed first by Levin [2] and then later by others [1, 3- 6] that alkali, and specifically Cs adatoms forming one-dimensional chains, reside on the raised sites of dimers of clean Si(100)2x1 [1,3 - 6]. Spiess et al. [7] support the one-dimensional chain for Na on Si(100)2x1, but they consider Na atoms only to be adsorbed on the cave sites. Recently, a double-layer model has been proposed by Abukawa and Kono [8], where the alkali

(cave site or valley bridge site), and provide a saturation coverage of of one monolayer, Θ = 1.The surface atomic density of 1 monolayer of Cs on Si(100)2x1 is considered equal to that of the outermost layer of Si, $N_{Si} = 6.8 \times 10^{14}$ atoms. cm^{-2}. The adsorptio of alkali on most metallic and semiconducting surfaces causes a decrease in work function which is interest in the making of thermionic energy converters [9 - 11]. The coadsorption of the electropositive alkali and elecronegative elements, such as oxygen, decreases further the work function of the surface and thus increasing the effciency of the thermionic emission of electrons. The sulfure is also an electronegative element and we thought that coadsorption of Cs ane S_2 on Si(100)2x1 would be interesting. This thought is favored by the recent important finding when elemental sulfur was deposited on clean the Si(100)2x1 surface [12]. Briefly, adsorption of elemental S at RT causes the transition of the reconstructed Si(100)2x1 surface to its original bulk-terminated Si(100)1x1. This transition takes place when Θs > 0.5 MLs. Above 1 ML sulfur is imbedded into the Si crystal . The S adsorbate is strongly bound to the Si substrate in a molecular Si-S form. We believe that Cs on a Si (100)2x1 surfaces passivated with S, may help the growth of Cs films greater than the single layer and reduce the work function of Cs on Si(100)2x1 further.

It is possible to control growth at the atomic level in certain systems with the proper choice of components and processing methods. The restoration of semiconductor surfaces to their original bulk-terminated surface has been achieved for different adsorbates. Specifically, ideal (1x1) terminations of (111) surface were reported for As on Si(111) [13, 14]. Moreover, a monolayer of As was used to successfully control the growth of the Ge overlayer on Si substrates [15]. When Ge is deposited on clean Si(100) it grows epitaxially for three monolayers, but then reverts to island growth. This is due to the lattice mismatch and the balance of surface and interface energies. A monolayer of As passivates the Si(100) surface. Arsenic keeps floating on top of the Ge during growth, allowing the pseudomorphic growth of considerably thicker Ge films, up to at least fifteen monolayers (15 MLs). More recently, group III atoms were used as surfactants during the growth of Ge on Si(111) [16]. The surfactants produce large changes in the surface energy of the Si surfaces.

In this work the adsorption of Cs on S-covered Si(100)2x1 surfaces is investigated. The properties of the above surface system has been studied using Auger electron spectroscopy (AES) and work function (WF) measurements. The kinetics and the mutual effects of Cs and S during their coadsorption on Si(100)2x1 have been discussed and are reported for the first time.

II.   Experimental

The experiments were performed in an ultra-high vacuum (UHV) chamber (p < 10^{-10} torr), equipped with a cylindrical mirror analyzer (CMA) for AES measurements and a Kelvin probe for WF measurements, the Si(100) substrate was cleaned by Ar+ bombardment at E=1 keV for 40 min with an ion current of 10 mA. After bombardment the sample was heated to 1000 °C by passing current through a 0.05 mm Ta strip,

uniformly pressed between the sample and a Ta foil case. The specimen temperature T_s was measured with a chromel-alumel thermocouple, spot welded onto the sample holder. Elemental sulfur was deposited by thermal dissociation of MoS_2 single crystal flakes mounted on a tungsten filament . During dissociation of MoS_2 the Mo remained on the tungsten filament while S was evaporated. The pressure was kept on the order of 10^{-10} torr as the S was deposited on the surface. The Cs deposition was done using a conventional alkali Getter source. The estimation of the S coverages on Si(100) surfaces were based on the reported results [12] in correlation with our AES and work function (WF) measurements.

III.   Results-Discussion

Auger measurements

As it is mentioned in the introduction, during deposition of S up to 0.5 MLs the recostructed S(100)2x1 surface is remained , whereas, with increasing S coverage above 0.5 ML the surface changes to a S(100)1x1 [12]. Based on this information we measure the Auger peak to peak hight of Cs(47 eV) versus Cs deposition doses on 0.5 MLs of S- covered Si(100)2x1 and on 1 ML of S- covered Si(100)1x1, as compared to that of Cs on clean Si(100)2x1, shown in Fig. 1.The Auger peak to peak height (Ap-pH) of Cs, at first, increases linearly up to the third dose of Cs. Between the third and fourth dose the slope of the Ap-pH vs Cs dose-curve decreases substantially. The new slope is nearly constant up to the ninth dose, where the Auger curve levels off, and the Cs coverage is saturated. We believe that at ninth dose the Cs saturates with a coverage of 1 ML (which has a density equal to the outermost layer of Si substrate) . The break near the fourth dose is attributed to different sites occupied by the Cs atoms before and after the break. Specifically, the Cs atoms are initially adsorbed on the dimer sites. After the completion of these sites, at fourth dose, the Cs atoms reside on the trough sites between the dimer rows. This is consistent with the double-layer model proposed by Abukawa and Kono (8). When Cs is deposited on S-covered Si surfaces, the Cs Auger peak heighr continues to increas up to our last measuremert, in contrast to that on clean Si surface which levels off near the completion of the first monolayer..A comparison of the Auger curves of Cs on S-covered Si(100) surfaces with that of Cs on clean Si(100)2x1 suggests that (a) the initial slope of the curve is the same in all cases independent of the presence and amount of the predeposited sulfur. This implies that the initial sticking coefficient of Cs on the Si(100)2x1 does not change in the presence of S on the surface and (b) the presence of predeposited sulfur on the Si(100)2x1 surface increases the maximum amount of the subsequently deposited Cs at RT above 1 ML, indepotently if the surface is reconstructed or not. .

Fig. 2 shows the Auger peak to peak height of Cs(47 eV) during heating temperature of Cs on the S-covered surfaces of Si(100) as compared to that of Cs on clean Si(100)2x1 surfaces. Cs is desorbed from the S-covered Si(100) in two steps: The first step occurs for values under 400 °C, and the second step for values over 400 °C. The Auger peak to peak height of Cs(47 eV) at 400 °C is close to that of a saturated Cs layer

on clean Si(100)2x1. This indicates that the Cs which is desorbed before 400 °C is bound to the second layer. The first Cs layer, i.e. the one directly bound to the substrate, is desorbed in the 400- 700 °C temperature range. There is a delay in the desorption of the Cs monolayer from the S-covered Si(100) surface as compared to Cs desorption from the clean Si(100)2x1 surface.This indicates that the presence of S on the surface increases the binding energy of Cs on the surface of Si. Probably this is the reason of increasing amount of Cs in the presence of S on the Si(100)2x1 surface.

Work Function Measurements

Figure 3 shows the work function change during Cs deposition (measured in doses) on clean Si(100)2x1, on 0.5 MLs of S-covered Si(100)2x1 and on 1 ML of S-covered Si(100)1x1 surfaces. Deposition of Cs on clean Si(100)2x1 initially decreases the WF to a minimum value Φ_{min} and subsequently increases again to a final maximum value, Φ_{max}. In the presence of the predeposited 0.5 MLs of S on Si(100)2x1, the WF minimum is even lower than that for Cs on clean Si(100)2x1, ($\Delta\Phi\sim$ 4.0 eV). The final WF increase is also smaller than that of Cs on clean Si(100)2x1. The initial decrease of the WF to Fmin during Cs deposition on the 1 ML of S-covered Si(100)1x1 is similar to that on 0.5 MLs of S. In the latter case, however, the Fmin value is maintained with the increasing amount of deposited Cs. In other words, during Cs deposition on the 1 ML of S-covered restored surface of Si(100)1x1, the WF decreases with Cs deposition, to a final plateau at the minimum value.

Figure 4 shows the work function change during heating temperature of Cs deposited on 0.5 MLs S-covered Si(100)2x1, and of Cs deposited on S-covered Si(100)1x1 surfaces as compare to that of Cs-covered clean Si(100)2x1 . The WF variation during heating is reversible, returning to the value it had during the deposition of Cs on the above surfaces at room temperature. The work function of clean Si(100)2x1 is reached at 700 °C when both Cs and S are completely removed. The information on the desorption of Cs from clean and S-covered surfaces of Si(100) is not substantially different compared to that of the Auger measurements (Fig. 2)

During Cs deposition on clean Si(100)2x1 the work function curve (Fig. 3) has the characteristic shape of the work function curves during Cs deposition on metals [17-20] and semiconductors [21]. These curves have an initial WF minimum Φ_{min}, and subsequently the WF increases with the tendency to reach the WF value of the metallic cesium (~2.1 eV) [19]. During the deposition of Cs on S-covered Si(100) surfaces both the Φ_{min} and the final maximum, Φ_{max}, decrease. When Cs is deposited on S(1 ML)-covered Si(100)2x1 the WF decreases to a minimum ($\Delta\Phi\sim$ 4 eV) value where the curve forms a plateau. Other semiconductors including some metal oxides also do not show the final WF increase [22-24]. The reported explanation is that in these cases the Cs overlayer is not in a metallic state, but probably in a covalent or ionic state [24]. Very similar are the reported results of Cs on oxygenated Ni(100) [25]. As the amount of the preadsorbed oxygen on the Ni(100) was increased, the final value of the WF was decreasing and when the Ni surface was oxidized the work function curve did not show the final increase, instead it exhibited a final plateau. This method was used to probe the oxide formation. In

the present case, the predeposited sulfur interacts strongly with the Si substrate, forming a Si-S complex analogous to NiO. The Cs overlayer on S(1 ML)-covered Si(100)1x1 surface is not metallic. It, more than likely, forms a covalent bond with the substrate. The final plateau at the work function minimum (<1 eV) was stable and probably appropriate for low work function devices (cathodes, thermionic energy conversion).

IV. Conclusion

In this work we describe the adsorption of Cs on clean reconstructed Si(100)2x1, on 0.5 MLs of S- covered Si(100)2x1, and on 1 ML of S- covered Si(100)1x1 surfaces at room temperature. The investigation takes place in ultra high vacuum (UHV) system with Auger electron spectroscopy (AES) and work function (WF) measurements. Adsorption of elemental sulfur above 0.5 MLs on clean Si(100)2x1 causus the restoration of the reconstructed Si(100)2x1 to Si(100)1x1surface (12). The saturation coverage of Cs on clean Si(100)2x1 surface at RT is 1ML. The presence of S on the Si(100)2x1 surface increases the binding energy and the maximum amount of the subseqently adsorbed Cs that can be deposited on the Si(100) surface at RT. Adsorption of Cs on clean Si(100)2x1 gives the characteristic work function curve of alkali on metals and most semiconductors, i.e. an initial minimum and subsequent increase towards the value of metallic Cs. Preadsorption of S on Si(100)2x1 further lowers the WF during subsequent Cs deposition by about 4 eV to a plateau without the final increase which,for alkali overlayers characteristic of metallization . This is consistent with a covalent bonding of S with the Si substrate. The stable minimum WF value of Cs on the S/Si(100) surfaces might be very interesting for low work function devices (cathodes, energy converters).

Acknowledgements

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*Corresponding author: Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, England.

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Figure caption

Figure 1. Auger peak to peak height of Cs(47 eV) on clean Si(100)2x1, on 0.5 MLs of S-covered Si(100)2x1 and on 1 ML of S- covered Si(100)1x1 versus Cs deposition doses.

Figure 2. Auger peak to peak height of Cs(47eV) versus temperature during the heating of Cs on clean Si(100)2x1, on 0.5 MLs of S- covered Si(100)2x1, and on 1 ML of S- covered Si(100)1x1.

Figure 3. Work function change during Cs deposition (measured in doses) on clean Si(100)2x1, on 0.5 MLs of S-covered Si(100)2x1 and 1 ML of S-covered Si(100)1x1 surfaces.

Figure 4. Work function change versus temperature during heating of Cs on clean Si(100)2x1, on 0.5 ML of S-covered Si(100)2x1, and on 1 ML of S-covered Si(100)1x1.
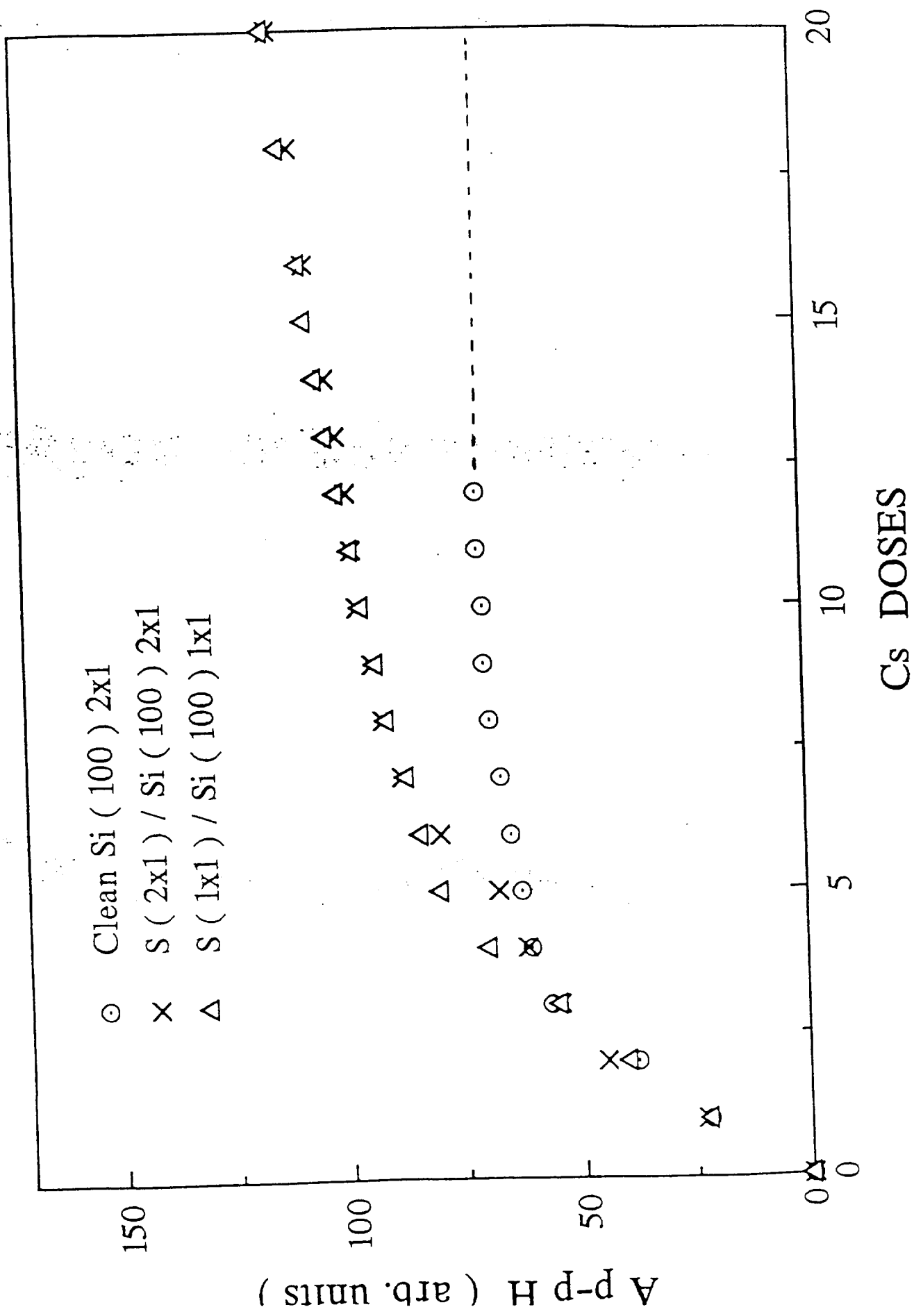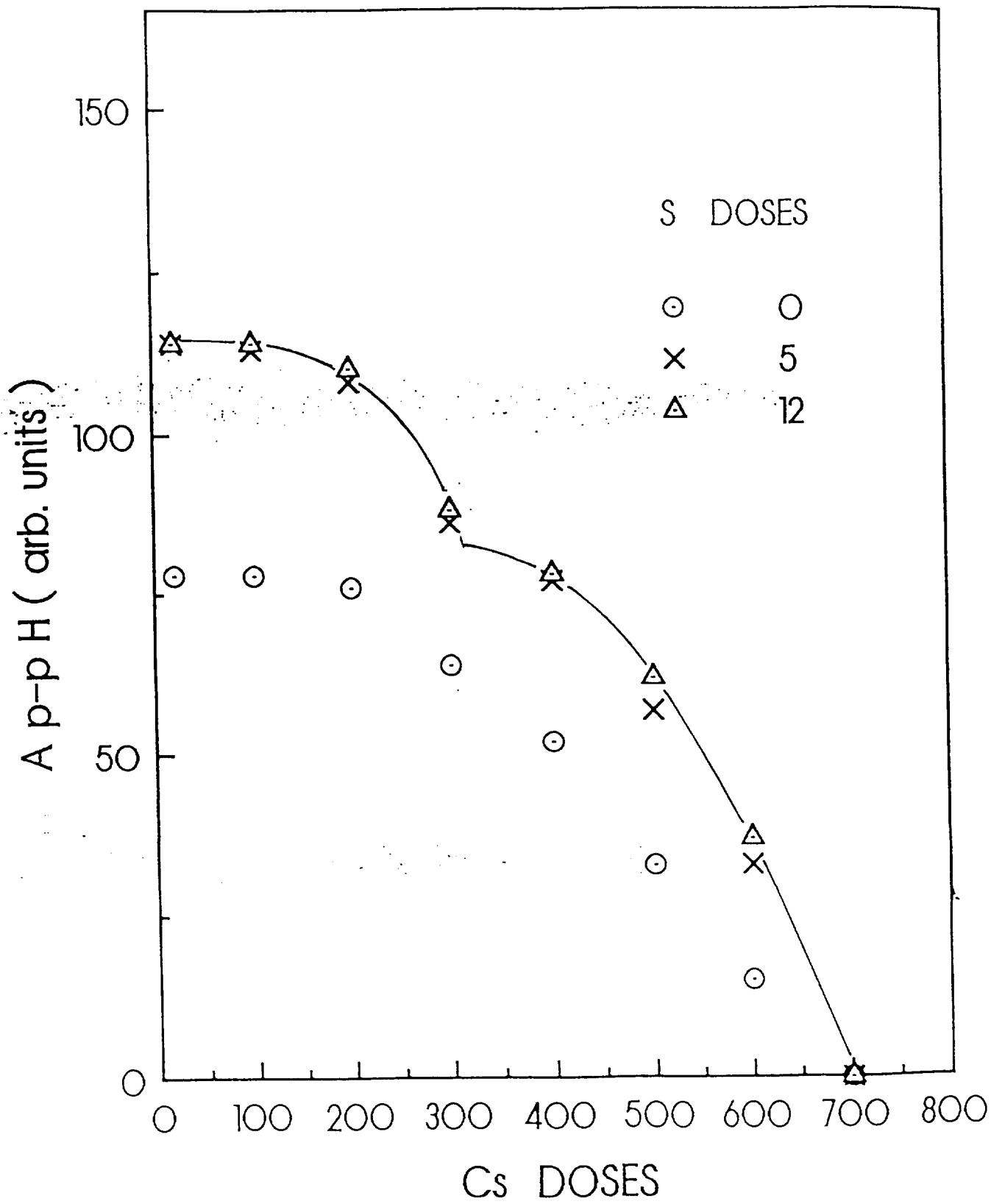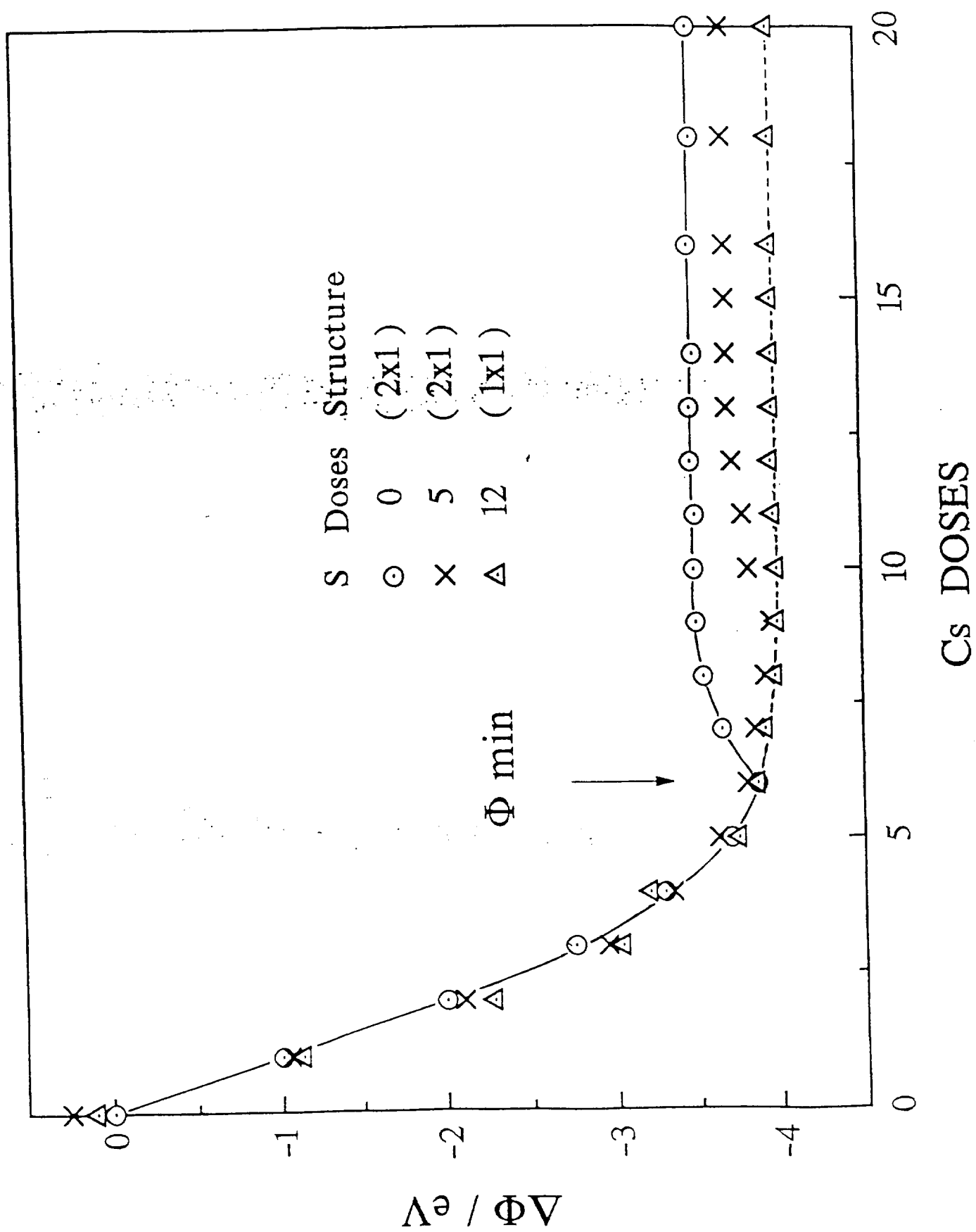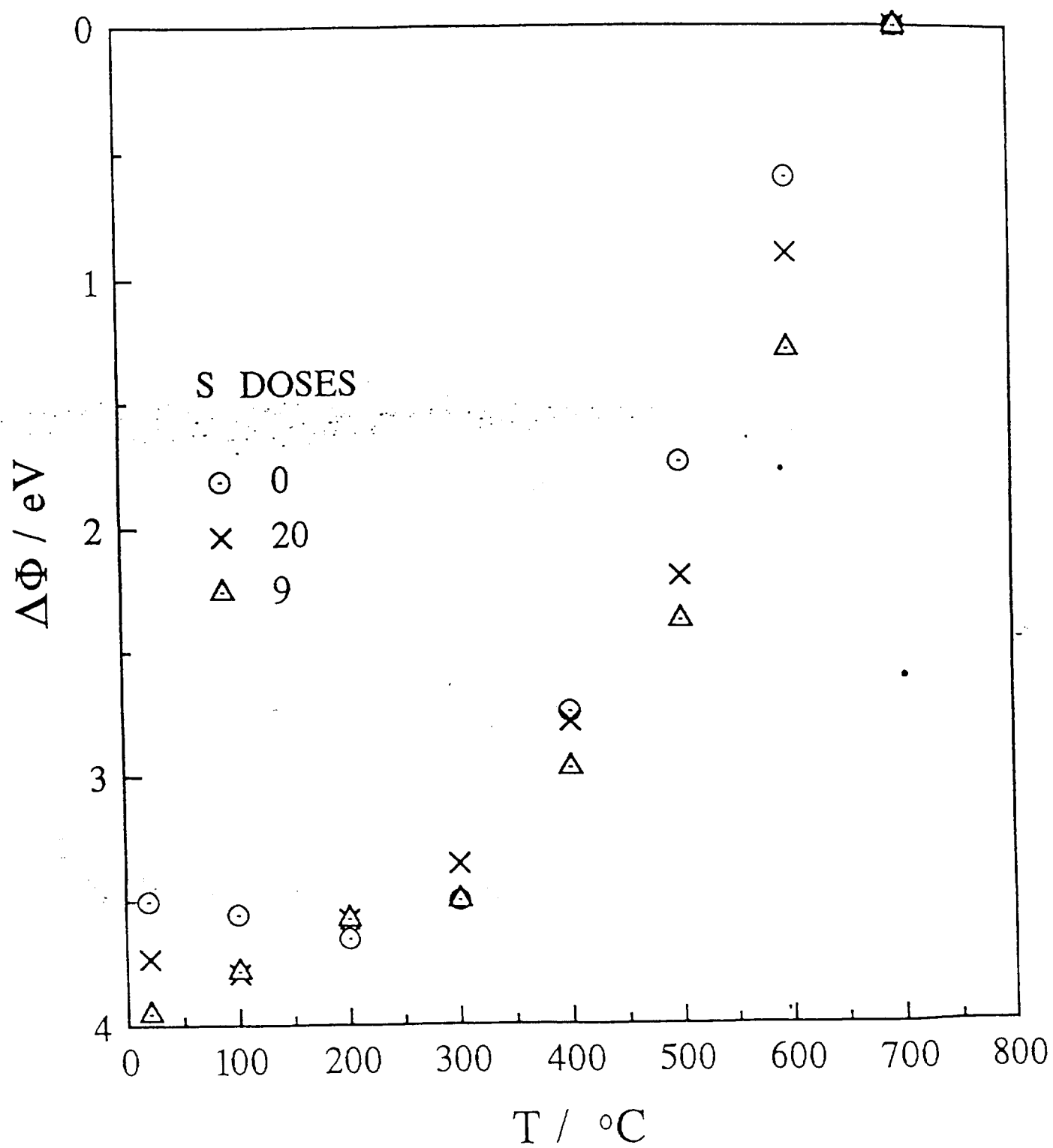
Cs DOSES

A p-p H (arb. units)

⊙ Clean Si (100) 2x1
× S (2x1) / Si (100) 2x1
△ S (1x1) / Si (100) 1x1

Fig. 2. Φ vs. Φ ...

(chart)

Axes: vertical axis labeled ΔΦ / eV, ranging from 0 to −4; horizontal axis labeled Cs DOSES, ranging from 0 to 20.

Legend:

S	Doses	Structure
⊙	0	(2x1)
×	5	(2x1)
△	12	(1x1)

Φ min →

S DOSES

⊙ 0
✕ 20
△ 9

Rcf 61

5th International Conference
on the Structure of Surfaces
July 8-12, 1996
Aix en Provence, France

Patrick Soukiassian
Professeur à l'Université de Paris-Sud/Orsay

Fax: (33) 1 69 08 35 92
Email: icsos@santamaria.saclay.cea.fr

Dr. C.A. Papageorgopoulos
University of Ioannina
Department Physics
P.O.Box 1186
GR 451 10 Ioannina
Greece

March 28, 1996

Dear Dr. Papageorgopoulos,

I am very pleased to inform you that the Program Committee has selected your following abstract for a 15 minutes Oral (12 minutes talk and 3 minutes for questions and discussion) presentation at ICSOS-5:

COADSORPTION OF ELEMENTAL S AND CS ON SI(100)2XL SURFACES

Aris Papageorgopoulos, 1 M. Kamaratos I and C. A. Papageorgopoulos 2
[1] Department of Physics and Center for High Performance Polymers and Ceramics, Clark Atlanta University, Atlanta, USA [2] Department of Physics, University of Ioannina, P.O Box 1186, GR - Ioannina, Greece

More than 400 abstracts have been submitted to ICSOS-5 and each abstract has been rated by two independent referees. Upon their evaluation, the Committee had to make very difficult decisions. Only very good contributions have been selected for presentation. This indicates the high level of ICSOS-5.

As a general rule, a speaker cannot present more than one oral presentation at ICSOS-5.

General instructions for manuscript preparation for the ICSOS-5 Proceedings to appear in Surface Review and Letters (SRL) are enclosed. Each submitted article will be refereed according to SRL standards. The manuscript should not exceed 4 printed pages of Surface Review and Letters meaning no more than 14,000 characters including title, abstract, text, references, figure captions, and 3 to 4 figures. Three copies of the manuscript should be submitted on Monday, July 8, 1996 at the ICSOS-5 Editorial Office in Aix en Provence.

Please find enclosed a Registration Form (Pre-Registration Dead Line: May 1, 1996) and a Hotel Reservation Form (Dead Line: May 1, 1996). Due to the large expected attendance, I urge you to make reservation and registration as soon as possible.

I am looking forward to seeing you in Aix en Provence.

Best Wishes

Yours sincerely

Patrick Soukiassian
Co-Chairman, ICSOS-5

Enclosures

The behavior of Cs on S-covered Si(100)2x1 and Si(100)1x1 surfaces

Aris Papagorgopoulos, Dwight Mosby

Department of Physics, Clark Atlanta University, Atlanta, Ga.,USA

C. A. Papageorgopoulos*

Department of Physics, University of Ioannina, P.O.Box 1186

GR-451 10 Ioannina, GREECE

Abstract

In this work we study the adsorption of Cs on (a) Clean Si(100)2x1 (b) 0.5 MLs of S-covered S(100)2x1 and (c) 1 ML of S-covered S(100)1x1 in ultra high vacuum (UHV). LEED and AES mesurements suggest that the array of a Cs monolayer clean and S-covered S(100)2x1 surfaces was that of the Double Layer model, according to which, half of the Cs atoms reside on the raised sites of the dimers and the other half in the trouphs. However, Cs on 1 ML of S-covered S(100)1x1 forms initially a coplanar monolayer with the Cs atoms residing only on one kind of sites. The presence of S on the Si surfaces inceases the subsequently deposited, at RT, coverage of Cs to more than one monolayer. Structural models of Cs on clean and S-covered Si(100) surfaces are proposed.

I. INTRODUCTION

The coadsorption of the electropositive alkali metals and electronegative elements on metallic and semiconductig substrates has been intensively studied in the past . Besides the theoretical interest on the coadsorption species, these systems have many considerable technological applications such as thermionic energy converters, microelectronics and photocathodes [1-3]. The sulfure is also an electronegative element and we thought that coadsorption of Cs ane S_2 on Si(100)2x1 would be interesting.This thought is favored by our recent important finding when elemental sulfur was deposited on clean the Si(100)2x1 surface [4]. Briefly, adsorption of elemental S at RT causes the transition of the reconstructed Si(100)2x1 surface to its original bulk-terminated Si(100)1x1. This transition takes place when the S coverage is > 0.5 MLs. Above 1 ML sulfur is imbedded into the Si crystal . The S adsorbate is strongly bound to the Si substrate in a molecular Si-S form.Similar restorations of recontructed (111) surface to its original bulk-terminated (1x1) surface were reported for As on Si(111) [5,6]. Moreover, a monolayer of As was used to successfully control the growth of the Ge overlayer on Si substrates [7].We believe that deposition of Cs on a Si (100)2x1 surfaces passivated with S, may help the growth of Cs films greater than the single layer and reduce the work function of Cs on Si(100)2x1 further. It is also interesting to study the electronic and structural properties of Cs overlayer on the (2x1) reconstructed and the ideal (1x1) surfaces of Si(100). There are different views pertaining to the nature of the bonding and the metallic character of the alkali adsorbate on Si(100)surfces [8-11]. Structural models have been proposed first by Levin [12] and then later by others [13,14-17] that alkali, and specifically Cs adatoms forming one-dimensional chains, reside on the raised sites of dimers of clean Si(100)2x1. Spiess et al [18] support the one-dimensional chain for Na on Si(100)2x1, but they consider Na atoms only to be adsorbed on the cave sites. Recently, a double-layer model has been proposed by Abukawa and Kono [19], where the alkali atoms are adsorbed on both the dimer sites and the trough sites

between the dimer rows (cave site or valley bridge site), and provide a saturation Cs coverage of one monolayer.The surface atomic density of 1 monolayer of Cs on Si(100)2x1 is considered equal to that of the outermost layer of Si, $N_{Si} = 6.8 \times 10^{14}$ atoms. cm^{-2}.

This study refers the adsorption of Cs on S-covered Si(100)2x1 surfaces is investigated. The properties of the above surface system has been studied using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) . The kinetics, the mutual effects and the structures of Cs and S during their coadsorption on Si(100)2x1 have been discussed and are reported.

II. *EXPERIMENTAL*

The experiments were performed in an ultra-high vacuum (UHV) chamber (p < 10^{-10} torr), equipped with a low energy electron diffraction (LEED) and a cylindrical mirror analyzer (CMA) for AES measurements. The Si(100) substrate was cleaned by Ar+ bombardment at E=1 keV for 40 min with an ion current of 10 mA. After bombardment the sample was heated to 1000 °C by passing current through a 0.05 mm Ta strip, uniformly pressed between the sample and a Ta foil case. The specimen temperature Ts was measured with a chromel-alumel thermocouple, spot welded onto the sample holder. Elemental sulfur was deposited by thermal dissociation of MoS_2 single crystal flakes mounted on a tungsten filament . During dissociation of MoS_2 the Mo remained on the tungsten filament while S was evaporated. The pressure was kept on the order of 10^{-10} torr as the S was deposited on the surface. The Cs deposition was done using a conventional alkali Getter source. The estimation of the S coverages on Si(100) surfaces were based on the reported results [4] in correlation with our AES and LEED measurements..

III. RESULTS

Fig. 1 shows the Auger peak to peak height of Cs(47 eV), S(151 eV) and Si(92 eV) vs Cs deposition on 1 ML of S-covered Si(100)2x1 surface, as compared to the Ap-pH of Cs (47 eV) vs Cs deposition on clean Si(100)2x1, shown with the dashed line.The Ap-pH of Cs on clean Si, at first, increases linearly up to the third dose of Cs. At the third dose the slope of the Ap-pH vs Cs dose-curve decreases substantially.The new slope is nearly constant up to the ninth dose, where the Auger curve levels off, and the Cs coverage is saturated. When Cs was deposited on 0.5 MLs of S-covered Si(100)2x1, the Auger peak (47 eV) curve forms also a break between the second and third dose of Cs, and a second break between the seventh and eighth dose. The Auger peak to peak height of Cs continues to increase with the increasing number of Cs doses above the ninth dose,when Cs saturates on the clean Si(100)2x1 surface. The two breaks are formed slightly earlier than those on clean Si. This is within the limits of the experimental error and we are not discussing. As it is shown in fig. 1 the Cs coverage on S/Si(100) does not saturate at the ninth dose, but it forms a second layer. The most surprising observation in fig. 1 is that the S(151 eV) peak height does not decrease with increasing coverage of Cs on S-covered Si(100)2x1. This may suggest that the deposited Cs atoms do not mask the preadsorbed atoms of sulfur.

Figure 2 shows the Auger peak to peak height of Cs(47 eV), S(151 eV) and Si(92 eV) versus Cs deposition on 1 ML of S-covered Si(100)1x1 surface. The preadsorbed monolayer of S then increases the maximum amount of subsequently deposited Cs even more than that of 0.5 ML of S. As in fig. 1, the S(151 eV) peak does not decrease with the increasing number of Cs doses. This may indicate that Cs and S adsorbates occupy independent surface sites beeing directly bound to the Si substrate. Possible displacement of S atoms to the top does not

agree with recent work function measurements (not shown here) The fig. 2, however, exhibits a substantial difference in comparison to the previous cases. The first break does not exist, while the second break appears near the fifth dose, when the first Cs layer is complited. This indicates that the adsorption sites and the nature of the binding energy are all the same within the first Cs layer on the restored S/Si(100)1x1 surface.

Adsorption of Cs on the clean Si(100)2x1 surface did not cause any substantial variation in the LEED pattern. In the early stages of Cs deposition on S-covered Si(100)2x1, the LEED pattern did not change substantially. The S structures, of the 0.5 MLs and 1ML or grater, remained with the underlying Si(100), retaining the (2x1) reconstruction in the first case and the (1x1) restoration in the second case. With increasing number of Cs doses above the completion of the first Cs layer the background increases substantially. Gradual increase of the temperature of the Cs/S/Si(100) surfaces initially decreases the background. In the case of the 0.5 MLs of S-covered on Si(100)2x1, the (2x1) pattern did not change; whereas, when the sulfur coverage was 1 ML on the restored Si(100)1x1, the (1x1) pattern changes to a (2x1) at about 550 °C. At this temperature, a substantial amount of sulfur is desorbed from the surface and the restored Si(100)1x1 structure changes back to the reconstructed Si(100)2x1.

IV. DISCUSSION

Based on a correlation of the existing literature, and our data we believe that the first break of the Auger curves (Fig. 1) is due to the different sites of Cs adatoms before and after the break. However, when Cs was deposited on 1 ML of S-covered restired S(100)1x1 surface we did not observe the fist break (fig. 2). This is reasonable because now all the sites are similar and the Cs atoms occupy the same kind of sites up to the competion of the first monolayer. Of course, above 1 ML, the Cs atoms forming an other layer change the slope of the Auger curve, which is characterstic of the layer by layer growth.The first monolayer of Cs atoms on the reconstructed surface forms a wave-like configuration, with the atoms of the initial 0.5 ML to reside on the raised sites of the dimers and the other half to reside deeper in the troughs. This array of the Cs atoms on Si(100)2x1 is actually the so called double-layer model, proposed by Abukawa and Kono[19]. According to this model the alkali atoms are adsorbed on both the dimer sites and the trough sites between the dimer rows and provide a saturation coverage of 1 ML. The Cs atoms, up to 0.5 ML, reside on pedestal sites, and over 0.5 ML rest on valley bridge sites. Since then, several experimental[20,21] and theoretical[22,23] investigations supported this model. The author feels that, during Cs deposition on 0.5 MLs of S-covered Si(100)2x1 surface, the Cs atoms reside on the same sites they occupied on clean Si(100)2x1. In this model the Cs atoms do not displace the predeposited S atoms which occupy different sites. The Cs atoms reside on the bridge sites between the dangling bonds (4). When Cs is deposited on 1 ML of S-covered Si(100)1x1 surface, all the Cs adatoms within the monolayer are on the same plane, and the nature of the binding is the same.Thus, the Cs and S atoms occupy different sites, without masking each other. This view is strongly supported by the Auger measurements (figs 1 and 2) where the S(151 eV) peak heights do not decrease with increasing amount of deposited Cs atoms on the S-covered Si(100) surface. In other words, the emitted Auger electrons from the S atoms do not cross the Cs atoms on their way out. Figs. 3 and 4, show schematic illustrations, side view and top view respectively,of the surface structure of a Cs monolayer on (a) a clean Si(100)2x1, (b) a 0.5 MLs of S-covered the reconstructed Si(100)2x1 and © a 1 ML-covered the restored Si(100)1x1 surface.The multilayer formation of Cs on Si(100) surfaces at RT is very interesting , beceause it well known that Cs forms only a single layer at RT on metals and semiconductors.
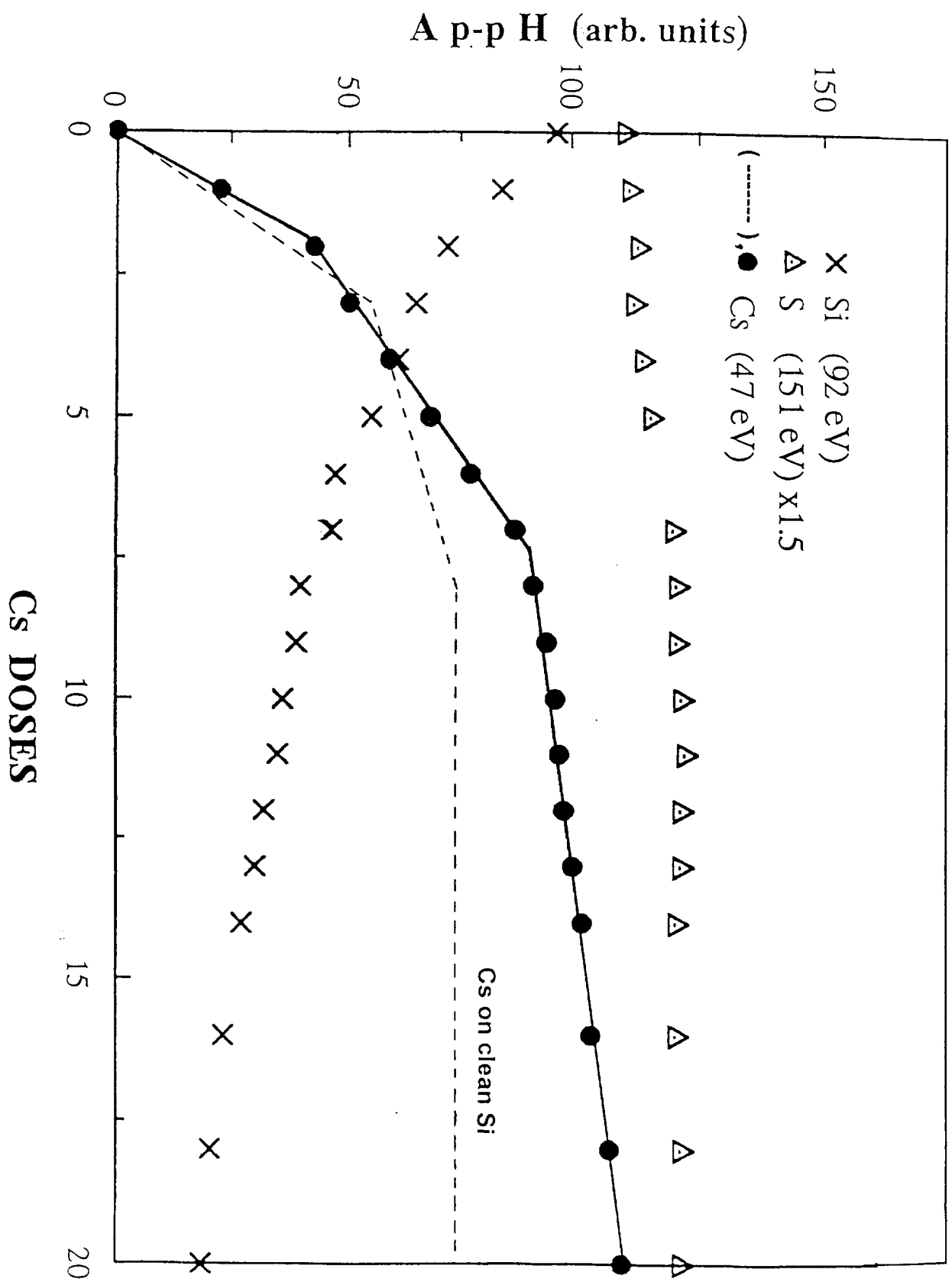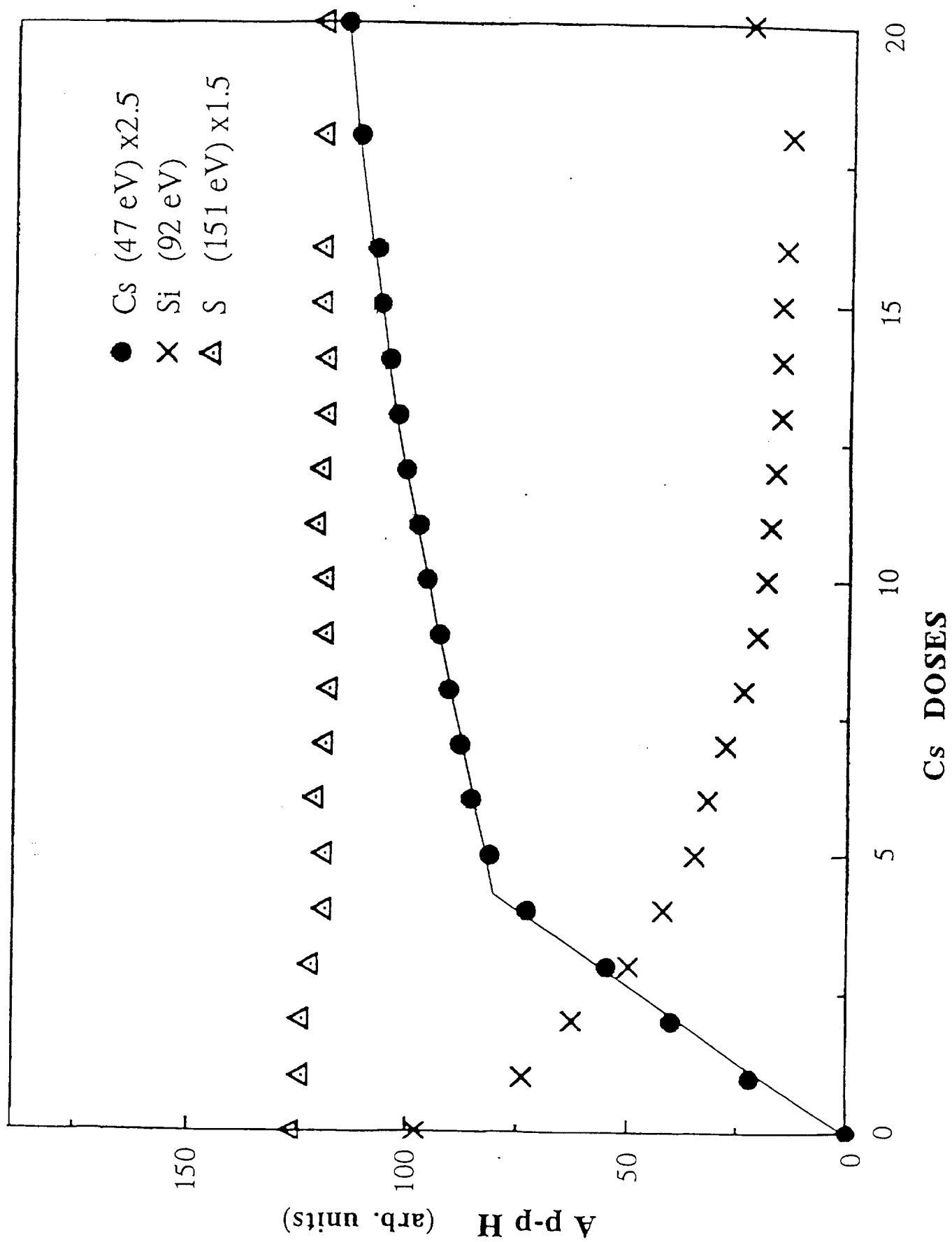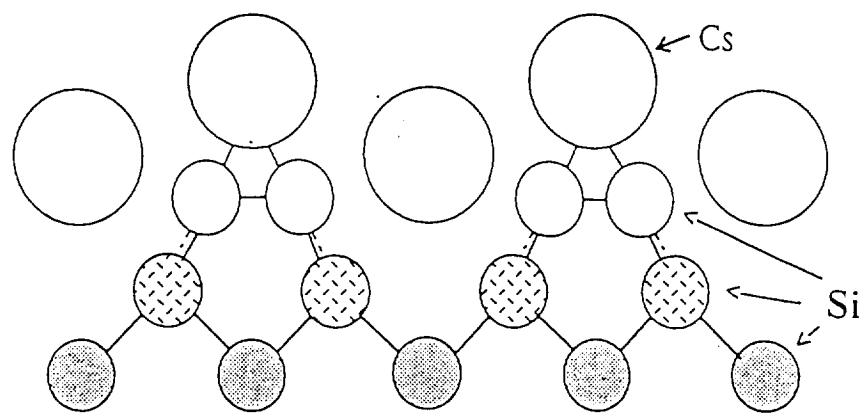
* Corresponding author

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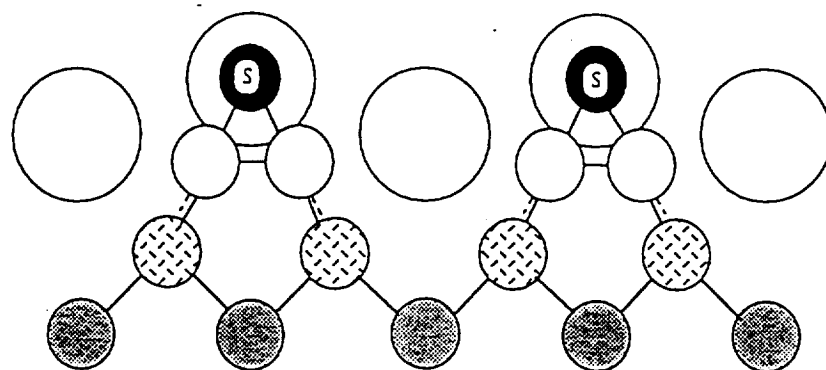
Figure Caption

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Figures. 3   Schematic illustrations of the side view of the surface structure of a Cs monolayer on (a) a clean Si(100)2x1, (b) a 0.5 MLs of S-covered the reconstructed Si(100)2x1 and © a 1 ML-covered the restored Si(100)1x1 surface.
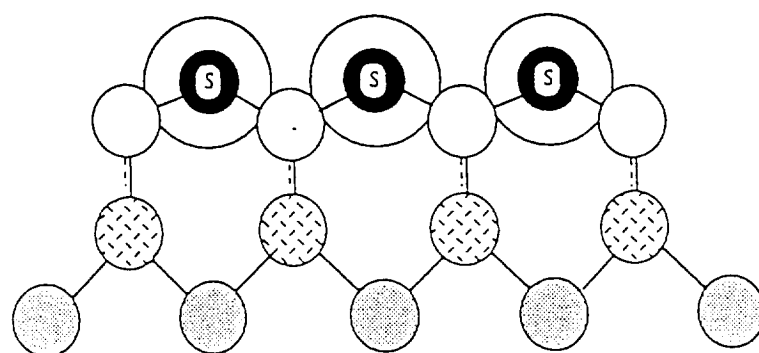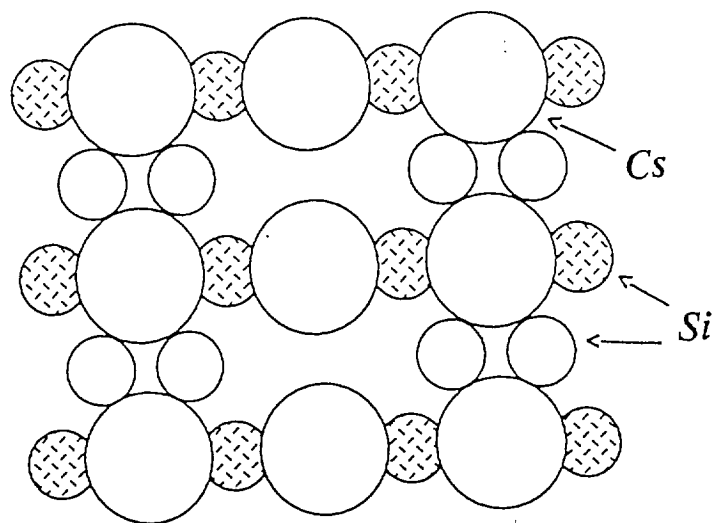
Figure. 4   Schematic illustrations of t the top view of of a Cs monolayer on (a) a clean Si(100)2x1, (b) a 0.5 MLs of S-covered the reconstructed Si(100)2x1 and © a 1 ML-covered the restored Si(100)1x1 surface
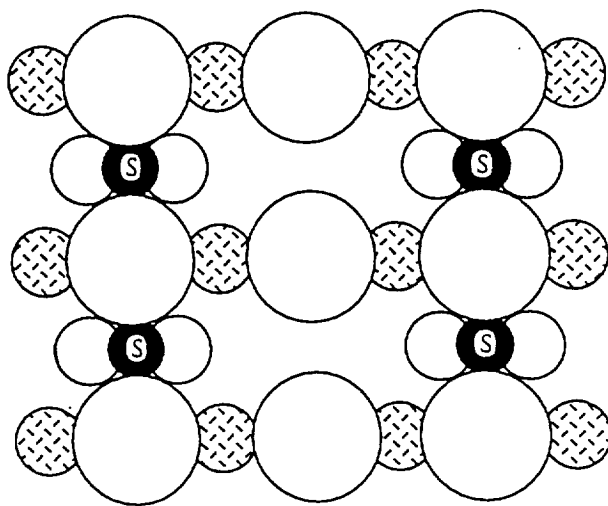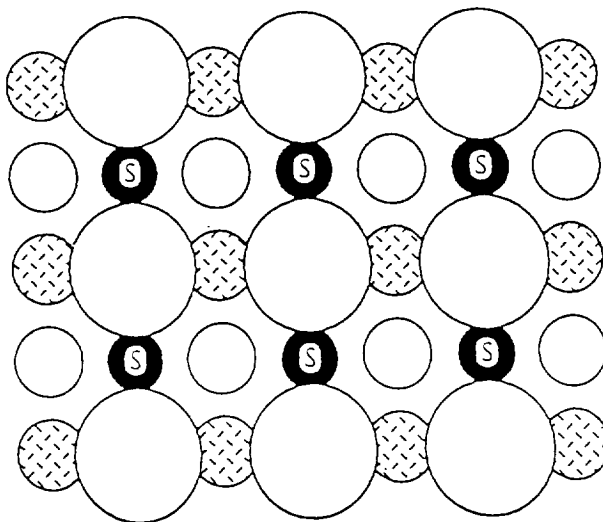
Cs (47 eV) x2.5
Si (92 eV)
S (151 eV) x1.5

Cs DOSES

A p-p H (arb. units)

(a)

(b)

(c)

Cs

Si

(a)

(b)

(c)