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ABSTRACT

The surface and interface properties of $Pd_{0.9}Cr_{0.1}$/SiC Schottky diode gas sensors both before and after annealing are investigated using Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS). At room temperature the alloy reacted with SiC and formed Pd_XSi only in a very narrow interfacial region. After annealing for 250 hours at 425 °C, the surface of the Schottky contact area has much less silicon and carbon contamination than that found on the surface of an annealed Pd/SiC structure. Pd_XSi formed at a broadened interface after annealing, but a significant layer of alloy film is still free of silicon and carbon. The chromium concentration with respect to palladium is quite uniform down to the deep interface region. A stable catalytic surface and a clean layer of $Pd_{0.9}Cr_{0.1}$ film are likely responsible for significantly improved device sensitivity.

INTRODUCTION

Palladium-based Schottky diode gas sensors using silicon carbide (SiC) as the semiconductor have demonstrated very high sensitivity to hydrogen and hydrocarbon gases at high temperatures. The simplest Pd-based SiC Schottky diode system is Pd directly deposited on SiC (Pd/SiC). Previous studies of the annealing effects on Pd/6H-SiC Schottky diode sensors indicated that the response of the diode to hydrogen degraded after annealing at 425 °C for 140 hours.[1] Surface and interface studies of an annealed diode showed that the annealing significantly promoted interfacial diffusion and chemical reactions; silicon dissociated from SiC diffused into whole Pd film region and formed silicides with palladium as the major interfacial products.[2] A significant amount of silicon oxide(s) and palladium silicide(s) also formed on the top surface of the contact area. These observations may explain the degradation of the device's response to hydrogen.

In this work we investigate the surface and interfacial properties of a $Pd_{0.9}Cr_{0.1}$/6H-SiC Schottky diode before and after annealing at 425 °C [3] using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Auger Electron Spectroscopy (AES). The diode is composed of a 400 angstrom (Å) $Pd_{0.9}Cr_{0.1}$ alloy film deposited on an n-type 6H-SiC epilayer which was grown on a 6H-SiC substrate. The electronic properties of these diodes are stable in comparison to the Pd/SiC diode. This work explores the interfacial composition and the spatial distributions of various constitutes at the interface region of both an as-deposited control sample and an annealed sample. The surface chemical composition and morphology of both the control and annealed $Pd_{0.9}Cr_{0.1}$/6H-SiC contact samples are investigated as well. The effects of the Cr component on the formation of the $Pd_{0.9}Cr_{0.1}$/6H-SiC interface at both room temperature and the elevated temperature are discussed according to the results of the surface and interface studies.

EXPERIMENT

Sample Fabrication and Gas Testing System

PdCr/6H-SiC Schottky diode sensors were fabricated using the same procedure discussed previously.[1] The epilayer was n-type doped with a donor (atomic) concentration of near $10^{16}/cm^3$ grown on a commercially available 3.5° off-axis polished C-face 6H-SiC substrate. The epilayer surface was etched by dilute HF solution, then rinsed with deionized water and blown dry by nitrogen immediately prior to vacuum loading for deposition of the $Pd_{0.9}Cr_{0.1}$ film. The surface of the epilayer could still be very slightly oxidized due to a short exposure in air. Approximately 400 Å of $Pd_{0.9}Cr_{0.1}$ alloy were magnetron-sputter deposited onto the epilayer using two targets simultaneously (Pd and Cr) to form a $Pd_{0.9}Cr_{0.1}$/SiC diode. The ratio of Pd to Cr was controlled by the relative power to the individual guns. The working gas was Ar and the deposition pressure was ~ 10^{-4} torr while the background pressure prior to Ar introduction was ~ 10^{-6} torr. The diode contact area was patterned by lift-off to delineate circular PdCr Schottky patterns of 200 μm diameter. A backside substrate contact was formed by sputtering aluminum (Al). The samples were mounted on a gold-coated alumina substrate positioned on a heating stage for gas tests and annealing. The heating stage was mounted in a test chamber and exposed to a variety of gas environments. The temperature of the heating stage was controlled from 100 °C to 425 °C. Computer controlled mass flow controllers supplied gaseous hydrogen (H_2), nitrogen (N_2), and air, either individually, or as a mixture, to the test chamber. However, the long-term annealing was carried out in air.

Surface and Interface Analysis

The surface and interface of both an as-deposited sample and a sample annealed in the manner discussed in the next section were studied by AES, SEM, and EDS. The AES system used for this work was a PHI-590 scanning AES (SAM) system with a single pass cylindrical mirror analyzer (CMA) and a coaxial electron gun. The relative energy resolution of the analyzer was set at 0.6%. The incident angle of the electron beam with respect to the sample surface normal was 60 degrees. The acquisition process of AES data (count of electrons vs. kinetic energy) was computer controlled, and the derivative spectra were obtained numerically. A positive argon ion beam with 4 keV beam energy was used for surface sputtering to obtain AES at various depths. The current density of the sputtering ion beam was 0.04 $\mu A/mm^2$ which corresponds to a sputtering rate of approximately 8 Å of PdCr per minute (min). Surface sputtering and acquisition of AES spectrum were conducted alternately. The pressure of the analysis system was in the low 10^{-7} torr range during sputtering while the pressure was in the high of 10^{-10} torr range during AES data acquisition. The SEM system used in this work is a SM-510 (TOPCON INTERNATIONAL) equipped with a LaB_6 filament, while the EDS system is a DX-4 (EDAX International) with an ECON4 windowless detector.

RESULTS AND DISCUSSION

Gas Testing

The electrical properties of a $Pd_{0.9}Cr_{0.1}$/SiC Schottky diode gas sensor have been characterized both before and after annealing, the results have also been discussed in reference 3. An as-deposited diode was first operated at 100 °C to establish stable electronic properties. Current-time (I-t) measurements at 0.7 V bias were taken as the sensor was exposed to 20 minutes of air, 20 minutes in nitrogen (N_2), 20 minutes of 120 ppm H_2 in N_2 (N_2/H_2 mix), 10

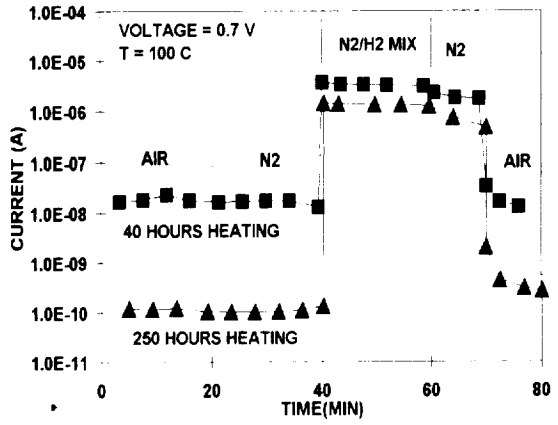

Figure 1: The forward current vs time at 100°C after 40 hours (■) and 250 hours (▲) heating at 425°C in air.

minutes of N_2, and then 10 minutes of air. The Schottky barrier height of the diode was measured in air and hydrogen via I-V measurements. After the baseline characteristics were measured, the diode was heat treated at 425 °C in air for periods of at least 13 hours. The diode was then characterized at 100 °C in the same manner used to establish the baseline. This cycle of heating followed by diode characterization was repeated until the total time of heating at 425 °C accumulated to 250 hours. Fig. 1 shows I-t data for various gas mixtures: the sensor baseline current in air is much lower after 250 hours of heating than at 40 hours, but the forward current in the N_2/H_2 mixture is the same within a factor of 3. Thus, the diode's sensitivity to H_2 is nearly two orders of magnitude larger at this bias after 250 hours of heating with a nearly stable response to H_2. This is in contrast to the behavior of a Pd/SiC diode[2] for which not only did the sensitivity decrease by an order of magnitude upon annealing for 140 hours at 425 °C but also the response to a given concentration of hydrogen degraded. The barrier height of the diode in air decreased with annealing time while the barrier height in hydrogen initially decreased and was then relatively stable after 40 hours of heating at 425 °C.[3] Therefore, the thermal stability of the $Pd_{0.9}Cr_{0.1}$/SiC diode is significantly improved compared to the Pd/SiC diode.

Surfaces

The surface of the Schottky contact area of the as-fabricated control sample is relatively clean and smooth. AES results shows that the surface of the contact area of the control sample contains only palladium, chromium, and some carbon and oxygen contamination but is free of silicon. The relative atomic concentration of chromium with respect to palladium is ~9.6%. SEM micrographs do not show any detectable surface structure at a magnification of 10000.

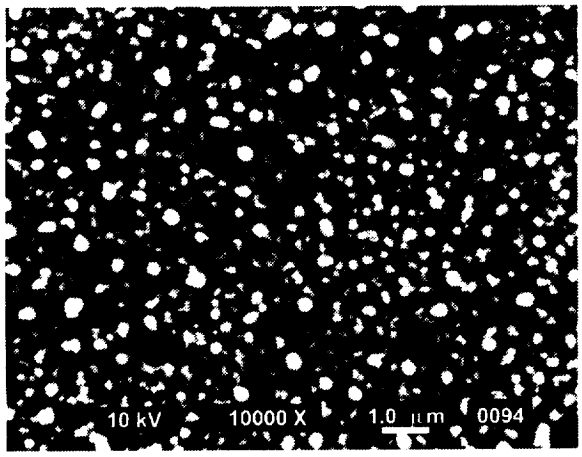

Figure 2: SEM micrograph of the contact area of a PdCr/SiC sample annealed for 250 hours at 425 °C. The surface normal of the sample was tilted 10 degrees from the electron beam.

A SEM micrograph, shown in Figure 2, of the Schottky contact area of the annealed sample described in the last section shows dense bright, irregularly shaped hillocks on a darker background. The lateral dimensions of these hillocks range up to ~0.5 micron. EDS measurements indicate that the relative concentration of palladium in the brighter hillock areas are much higher than that of the dark background, so the contrast is basically elemental rather than topographical.

AES results for the surface of Schottky contact area of the annealed sample indicate that the silicon, carbon, and oxygen contamination are low compared with those of annealed Pd/SiC sample.[2] AES detects palladium, silicon, chromium, oxygen, carbon, and some sulfur

(segregated from the alloy film as an impurity). The relative atomic concentrations of silicon, palladium, chromium, oxygen, and carbon are 15.1%, 55.2%, 9.3%, 20.3%, and less than 1%, respectively. In contrast, the Si concentration with respect to palladium on the surface of the annealed Pd/SiC is more than 60%. The relative chromium concentration with respect to palladium is 14.5% which, as will be seen in the next section, is high compared with the subsurface region. The third LMM chromium Auger peak shifts from 571 eV (the metal state) to 573 eV (see the discussion in the next section) with an oxygen presence on the surface. This indicates that the chromium on the surface is oxidized. These results suggest the presence of a clean catalytic surface which is extremely important for maintaining the high efficiency of hydrogen and hydrocarbons dissociation on the device surface.[2]

Subsurface Regions

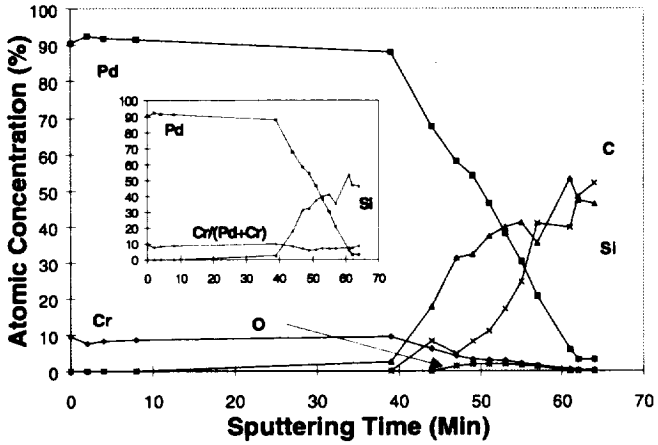

Figure 3: Concentration depth profile of control $Pd_{0.9}Cr_{0.1}$/SiC sample. Carbon and oxygen are not included in the surface concentrations (t=0). The data labeled as Cr/(Cr+Pd) in the inset shows Cr concentration of PdCr alloy for the same data.

The concentration depth profile of the control sample is shown in Figure 3. Chromium slightly segregated to the surface, but the chromium distribution in the whole alloy film is basically uniform down to the deep interface region as shown in the inset of Figure 3. The alloy film is free of silicon and carbon. In comparison with the depth profile of a Pd/SiC sample,[2] the interface is relatively narrow and sharp. The oxygen in the interface region may be from the residual surface adsorbate on the SiC substrate. Even though the oxygen content inside the film (10 min < t < 35 min, t is the accumulated sputtering time in min) is low, the third Auger peak of the chromium LMM transitions shows a shift from 571 eV (the metal state) to 573 eV, which is an indication of an oxidized state (losing electrons). This may indicate that chromium is chemically bound with palladium. The increase of carbon concentration with depth at the interface region is retarded with respect to that of silicon. This indicates that at room temperature the interfacial mixture and reactions are largely caused by diffusion of silicon dissociated from SiC into the alloy film rather than alloy diffusion into the SiC substrate. In the interfacial region, AES of Si $L_{2,3}VV$ transitions show features at 76, 84.5, 89, and 91 eV, which are strong indications of the formation of palladium silicides.[2, 4] It has been reported that chromium forms carbides with silicon carbide at the Cr/Si-face-6H-SiC interface,[5] as indicated by interfacial carbon KLL Auger spectra. However, we did not observed any similar evidence of formation of carbide at the interface of the $Pd_{0.9}Cr_{0.1}$/C-face-6H-SiC control sample. It is worthwhile to point out that carbide features of carbon KLL transitions could have been missed in our case due to the relative low chromium concentration with respect to carbon and/or the overlap of carbon KLL features with those of the palladium $M_{4,5}N_{2,3}V$ transition.

The concentration depth profile of the annealed sample is shown in Figure 4. The inset of Figure 4 shows the chromium concentration with respect to palladium at various depths. The chromium concentration (with respect to Pd) decreases sharply from 14.5% to 10.4% within the first 3 min of sputtering. This indicates that heating promoted chromium segregation to the alloy

surface. The surface silicon concentration is ~15%, but it decreases sharply with depth as shown in Figure 4. As was discussed previously, the surface silicon may have resulted from both segregation of impurity silicon in the metal film and quasi two dimensional diffusion of silicon dissociated from the SiC surface.[2] In the region corresponding to 10 min < t < 25 min, the silicon and carbon concentration levels were close to zero so this part of the alloy film is still clean after annealing. In this region the chromium concentrations with respect to both palladium and the sum of all elements (Pd, Si, O, C) are relatively higher compared to the deeper region beginning at t ~ 25 min. At t ~ 25 min , the silicon (palladium) concentration has a sharp increase (decrease). The low silicon and carbon concentrations in the 10 min < t < 25 min region are apparently correlated to higher relative chromium concentration with respect to palladium. Even though it is not yet clear whether the diffusion process of silicon and carbon towards the alloy film has stopped (or largely slowed down) at this depth after 250 hours annealing at 425 °C, the sharp edge of the silicon distribution does not look like a exponential tail resulting from quasi one dimensional diffusion.

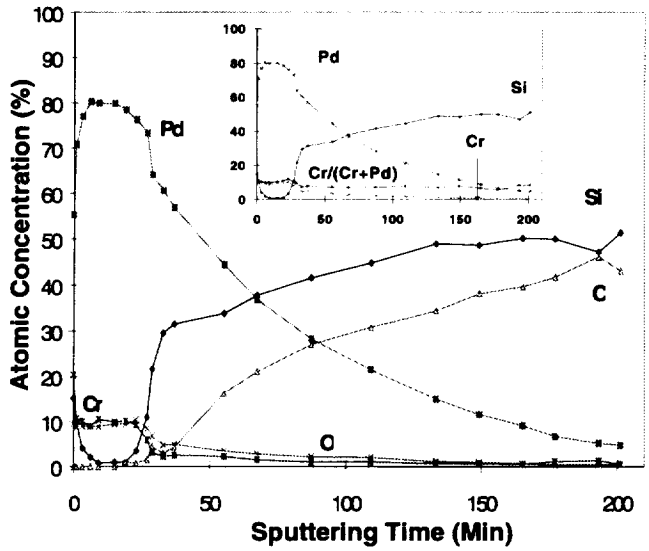

Figure 4: Concentration depth profile of annealed $Pd_{0.9}Cr_{0.1}$/SiC sample. The data labeled as Cr/(Pd+Cr) in the inset represents the chromium concentration of PdCr alloy for the same data.

At the depth t = 29.3 min , where there is a little hump in the carbon concentration profile and silicon concentration starts to increase, the AES of the carbon KLL transition shows carbide features. It is not completely clear if chromium formed carbide in this region. In the region, 35 min < t < 200 min, the concentration data show normal distributions resulting from interfacial diffusion. In this region it is noted that the chromium concentration with respect to palladium is relatively lower than those in the upper region, as shown in inset of Figure 4. Since the chromium concentrations are much lower than those of carbon, even if chromium carbide has formed, the carbide features of the carbon KLL spectra are not expected to be visible. In the whole depth profiled region, the distribution of oxygen basically follows that of chromium, this trend suggests the possibility that at least some chromium is bound to oxygen during the annealing process. However, the detailed chemical relations between chromium, palladium, and oxygen are not yet completely understood.

According to these results, both interfacial diffusion and chemical reactions were significantly promoted at 425 °C, changing both the interface region and interfacial products during the annealing process. The changes in interfacial constituents and their distribution directly affect the Schottky barrier height of the device which in turn effects the sensitivity to hydrogen. The formation of palladium silicides near the interface may decrease hydrogen solubility at the effective metal/semiconductor interface thus lowering the device response to hydrogen. However, the $Pd_{0.9}Cr_{0.1}$/SiC diode still shows a clean alloy region after annealing. This indicates that the diffusion and reactions at the $Pd_{0.9}Cr_{0.1}$/SiC interface are significantly slowed down exhibiting an improved thermal stability of the interface compared to that of the Pd/SiC interface.

SUMMARY

The thermal stability of both the electronic and interfacial properties of a $Pd_{0.9}Cr_{0.1}$/6H-SiC diode is improved compared to that of a Pd/SiC diode. The response of $Pd_{0.9}Cr_{0.1}$/6H-SiC diode to hydrogen is almost stable after 40 hours of heating at 425 °C and the sensitivity of the device to hydrogen increases. At room temperature, palladium silicides formed in a relatively narrow interface region and the majority of the PdCr alloy film is clean. After annealing for 250 hours at 425 °C, the surface of $Pd_{0.9}Cr_{0.1}$/6H-SiC contact area still has a low silicon content compared with that of annealed Pd/SiC structure, and a significant portion (layer) of the PdCr alloy film is still free of silicon and carbon. In the clean portion of the annealed film, the chromium concentration is unchanged and higher than the region with silicide formation. A catalytic surface with less contamination and an interface with improved thermal stability are responsible for the excellent sensor performance after annealing.

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