On the Sputtering of Binary Compounds*

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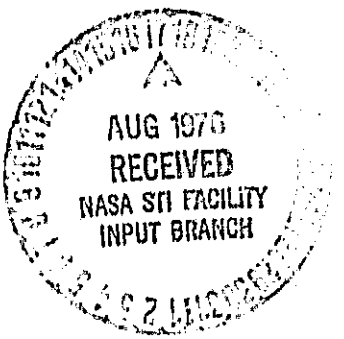

ABSTRACT

A simple physical model is presented to describe some aspects of the sputtering of compound targets. In particular, expressions are developed for the partial sputtering yields for binary systems in terms of the elemental sputtering rates, the stoichiometric concentrations and surface binding energy. The partial yields depend non-linearly on the bulk target concentrations. Comparison of the theoretical predictions with the data on sputtering of PtSi, NiSi and Cu_3Au indicates that the general features are well described.

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*Supported in part by the National Science Foundation [PHY76-02724], the National Aeronautics and Space Administration [NGR 05-002-333] and the Ford Motor Company at the California Institute of Technology.

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In recent years there has been increasing attention directed towards studies of the sputtering of complex materials. Investigations of metal alloys have indicated that, at least for those cases where more than a few atomic layers are removed, sputtering proceeds at a rate which bears no obvious relationship to the sputtering rates of the individual constituents.[1,2] In addition, while the composition of the sputtered material closely reflects the bulk composition of the target, the surface layer undergoes differentiation during bombardment.[2-8] Studies of the behavior of SiO_2 under Ar irradiation have pointed to similar conclusions.[9]

At the present time there exists no theory which predicts the partial sputtering yields of the individual constituents of a compound target. In this paper we address this particular aspect of binary sputtering through the use of physical arguments similar to those used to describe the sputtering of elemental targets. Comparison of the model predictions are then made with recent data of Poate et al.[2] for sputtering of PtSi and NiSi as well as the measurements of Ogar et al.[1] on Cu_3Au.

In the standard picture of sputtering of elemental targets, a beam-target collision produces a primary recoil atom which induces a cascade of low energy secondaries, some of which escape through the target surface and comprise the sputtering yield. Both the probability for the initial collision to occur near the surface and the average number of low energy secondary recoils are quantities proportional to the number density of target atoms. In a binary target composed of species a and b with abundances n_a and n_b, respectively ($n_a + n_b = 1$) the partial sputtering yield of a is therefore expressible in terms of the abundances and elemental sputtering yields as the sum[10]

$$S_a(n_a) = n_a n_a S_a(1) + n_a n_b S_b(1) \quad . \tag{1}$$

In accordance with the picture referred to above, the first term accounts for sputtered a-atoms ultimately derived from beam-a collisions, and the second term accounts for those sputtered a-atoms having their origin in beam-b collisions.

Here we have made the important assumption that the fraction of a-atoms contributing to the secondary cascade is just the stoichiometric fraction n_a, and similarly for species b. Different atomic masses in the target can, in general, lead to non-stoichiometric effects. However, Andersen and Sigmund[11] have studied this problem in detail and, while no simple rules seem to emerge, find that deviations from stoichiometry are significant only for cases of extreme mass ratios, as exemplified by uranium carbide.

Actually, in most sputtering theories the yield from an elemental target is inversely proportional to a surface binding energy U. This quantity depends upon the target structure. In eq. (1) we may allow for this feature by multiplying $S_a(1)$, $S_b(1)$ by the corresponding elemental surface energies, and then dividing by a similar quantity characteristic of the composition of the compound target,

$$S_a(n_a) = \frac{n_a}{U_a(n_a)} \left[n_a U_a(1) S_a(1) + n_b U_b(1) S_b(1) \right] \quad . \tag{2}$$

A similar equation holds for $S_b(n_b)$.

The function $U_a(n_a)$ is not known, in general, and if fitted to experiment, its empirical value would reflect not only changes in binding energy induced by alloying, but also the effects of the various approximations we

have made. On the other hand, we will see that the value determined in this way is rather independent of the bombarding energy and projectile — as it should be if it reflects a purely target characteristic — and furthermore, does not become so extremely large or small that its interpretation as a surface energy (≈ few eV) becomes untenable.

The total sputtering yield $S_{tot}(n_a)$ then becomes

$$S_{tot}(n_a) = S_a(n_a) + S_b(n_b) \quad . \tag{3}$$

If we take $U_a(n_a) = U_b(n_b) = U$, then

$$S_{tot(n_a)} = \frac{1}{U}\left[n_a U_a(1) S_a(1) + n_b U_b(1) S_b(1)\right] \quad . \tag{4}$$

Within the assumption of equivalent surface binding energy for a and b, the sputtering is predicted to be stoichiometric, as observed experimentally. Although eq. (4) bears some similarity to models in which the total sputtering yield is constructed from partial yields postulated to be of the form $S_i(n_i) = n_i S_i(1)$, the physical arguments adduced above show that this approach is misleading.

To illustrate the behavior implied by eq. (2), we plot in Fig. (1) the ratio of sputtering rates in an alloy to that of the element as a function of composition for the case of a PtSi target. All values of U were set equal, so that the variation evident in the figure arises from the explicit non-linear abundance factors in eq. (2). The fact that $S_{\overline{PtSi}}$ may become higher than S_{Si} (in this example, when $n_{Si} \geq 0.6$) emphasizes that addition of Pt to Si results in more efficient extraction of energy out of the beam near the target surface.

Recently published data[2] for Ar sputtering of PtSi and NiSi are

presented in Table I and it is seen, for example, that the ratio of the alloy to elemental sputtering rates are in disagreement with the calculation of Fig. 1. Within the context of our model this is clearly due to the fact that we have set all values of U equal. In order, therefore, that calculations of $S_{tot}(PtSi)$ fit the observed value at 20 keV, a value of $U_{Si}(\frac{1}{2}) = U_{Pt}(\frac{1}{2}) = 3.3$ eV was used and may be compared to the unalloyed values[12] $U_{Pt}(1) = 5.9$ eV, $U_{Si}(1) = 4.7$ eV. This choice of 3.3 eV gives excellent agreement with the experimental partial sputtering yields. Moreover, with this same choice, the 900 eV data are well reproduced and preserving the same value for U ($U_{Ni}(1) = 4.5$ eV, for comparison) also produces good agreement with the 20 keV measurements on NiSi.

With respect to the data of Ogar et al.[1] on the sputtering by Hg and Ar of Cu_3Au, we show in Fig. 2 a comparison of calculated energy dependence of partial sputtering yields of Au and Cu under Hg bombardment with the measurements. Normalizing the theoretical curve to the 10 keV point (requiring a value of U which is $\approx 65\%$ of the average elemental values), results in rather good overall agreement except at the 14 keV point. With the same choice of U, the predicted partial yields of Au and Cu under Ar bombardment are about 30% higher than measured, possibly indicating the degree to which U may be interpreted as reflecting solely a change in the surface energy.

Although it has not been possible within the simple model outlined here to accomodate effects of composition changes at the surface of alloys,[2-8] we feel that the sequence of physical events summarized in eqs. (2) and (4) is an important characteristic of sputtering in binary systems. Our approach, therefore, has been to try to expose these salient features in a manner consistent with the observation of stoichiometry in the sputtering

yield. In order to verify the validity of this approach, in a way that minimizes parameter adjustments, it would be valuable to have data on alloy sputtering at fixed bulk concentrations as a function of projectile and beam energy. For instance, in the case studied by Poate et al.[2] of PtSi the ratio of $S_{Pt\overline{Si}}/S_{Si}$ is predicted to increase from the measured value of 1.6 at 20 keV to ≈ 3 at 1 MeV Ar energy if one extrapolates the elemental rates, S_{Pt} and S_{Si}, with Sigmund's formulae.[13] $S_{\overline{Pt}Si}/S_{Pt}$ is expected to decrease only slightly (≈ 10%) over this energy range.

In conclusion, we have presented physical arguments which extend the usual theory of elemental sputtering to the case of binary targets. The contribution to the partial sputtering yield of one species is seen to be closely connected to the elemental sputtering yields of both species. The partial yields do not scale linearly with abundance, but may be either greater or less than a stoichiometric scaling would predict. An adjustable parameter of the model is interpreted as a modified surface binding energy, and some experiments are suggested which do not require an adjustment of this parameter to effect a comparison. The model is shown to reproduce qualitatively the observed tendency for sputtering of Si in PtSi and Cu in Cu_3Au to occur at rates higher than their stoichiometry suggests, and when the model is normalized at one bombarding energy, it reproduces the partial yields at other energies reasonably well.

We very much appreciate encouraging comments from Drs. J. Mayer and J. Poate. We are especially grateful to Professor T. A. Tombrello whose enthusiastic support and advice stimulated our thoughts in this work.

Table I

Ar-Sputteri[illegible] f PtSi and NiSi

	900 eV		20 keV	
	expt.[a]	theory	expt.[a]	theory
S_{Pt}	1.7		4.1	
$S_{\overline{PtSi}}/S_{Pt}$	0.50	0.52	0.54	0.54[b]
S_{Si}	0.52		1.5	
$S_{Pt\overline{Si}}/S_{Si}$	1.77	1.85	1.67	1.61
S_{Ni}			4.9	
$S_{Ni\overline{Si}}/S_{Si}$			1.47	1.49
$S_{\overline{NiSi}}/S_{Ni}$			0.45	0.44

[a]Data are taken from Poate et al.[2]

[b]Theory normalized to this point giving U = 3.3 eV. In the calculations, the following compositions, noted by Poate et al.,[2] were used: $PtSi_{1.1}$ and $NiSi_{1.05}$.

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Figure Captions

Fig. 1. Variation of partial sputtering rate with composition. The ratio of the sputtering of the components in a Pt-Si alloy to their elemental rates are shown as the dashed curves for the case of sputtering by 20 keV Ar (where $S_{Si}(1) = 1.5$ and $S_{Pt}(1) = 4.1$ ref.[2]). The solid lines reflect a simple stoichiometric variation.

Fig. 2. Energy dependence of sputtering yields of Cu, Au and Cu_3Au under Hg bombardment. The curves for Cu and Au were calculated with Sigmund's formalism[13] (with $U_{Cu} = 3.5$ eV, $U_{Au} = 3.8$ eV) and agree well with published data for sputtering of the (100) metals at normal incidence (see references quoted in ref.[1]). The dashed curves are the predictions of eq. (2) with $U = 2.35$ eV. The data points were taken from Fig. 1 of Ogar et al.[1]

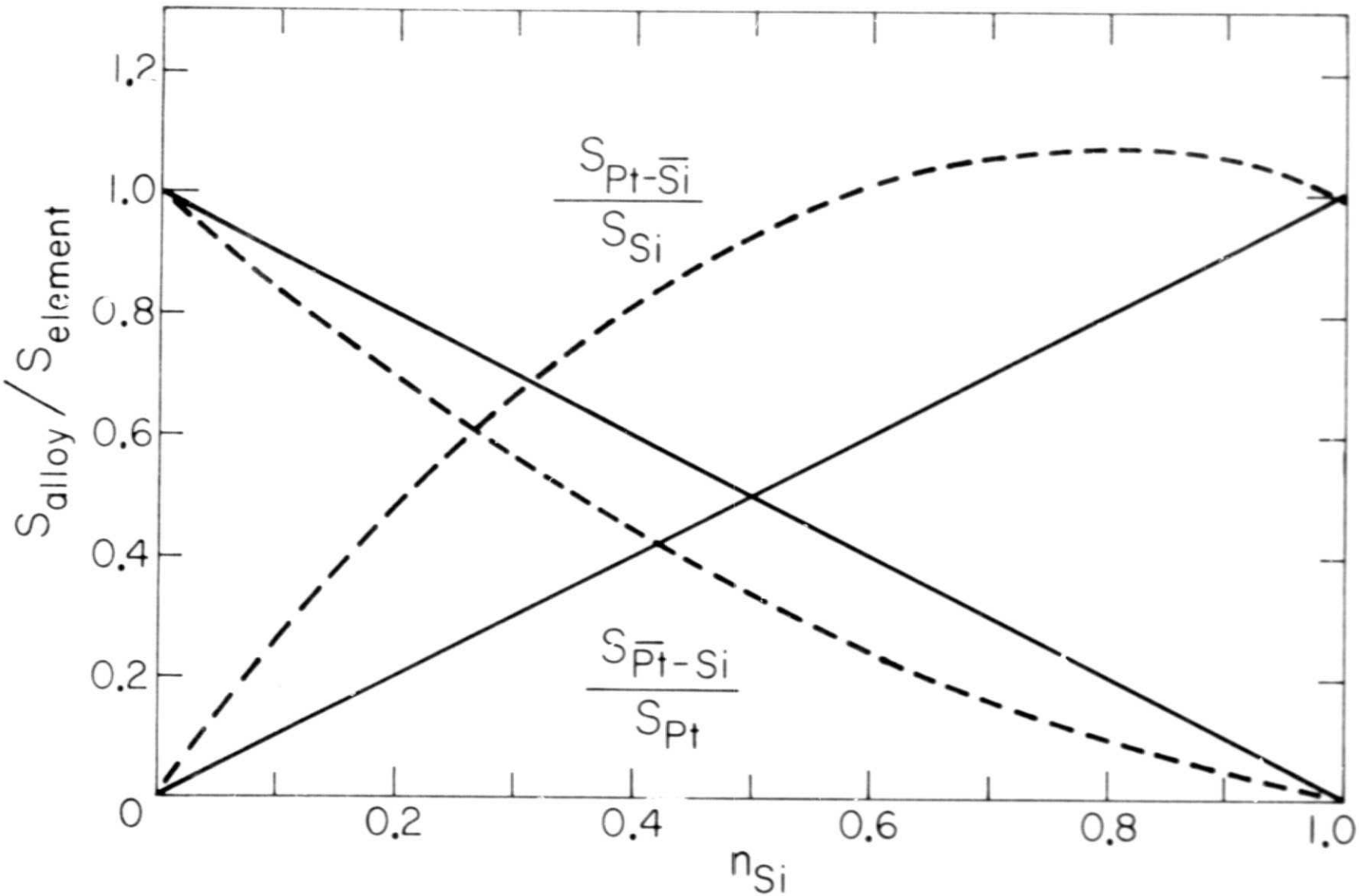

Fig. 1

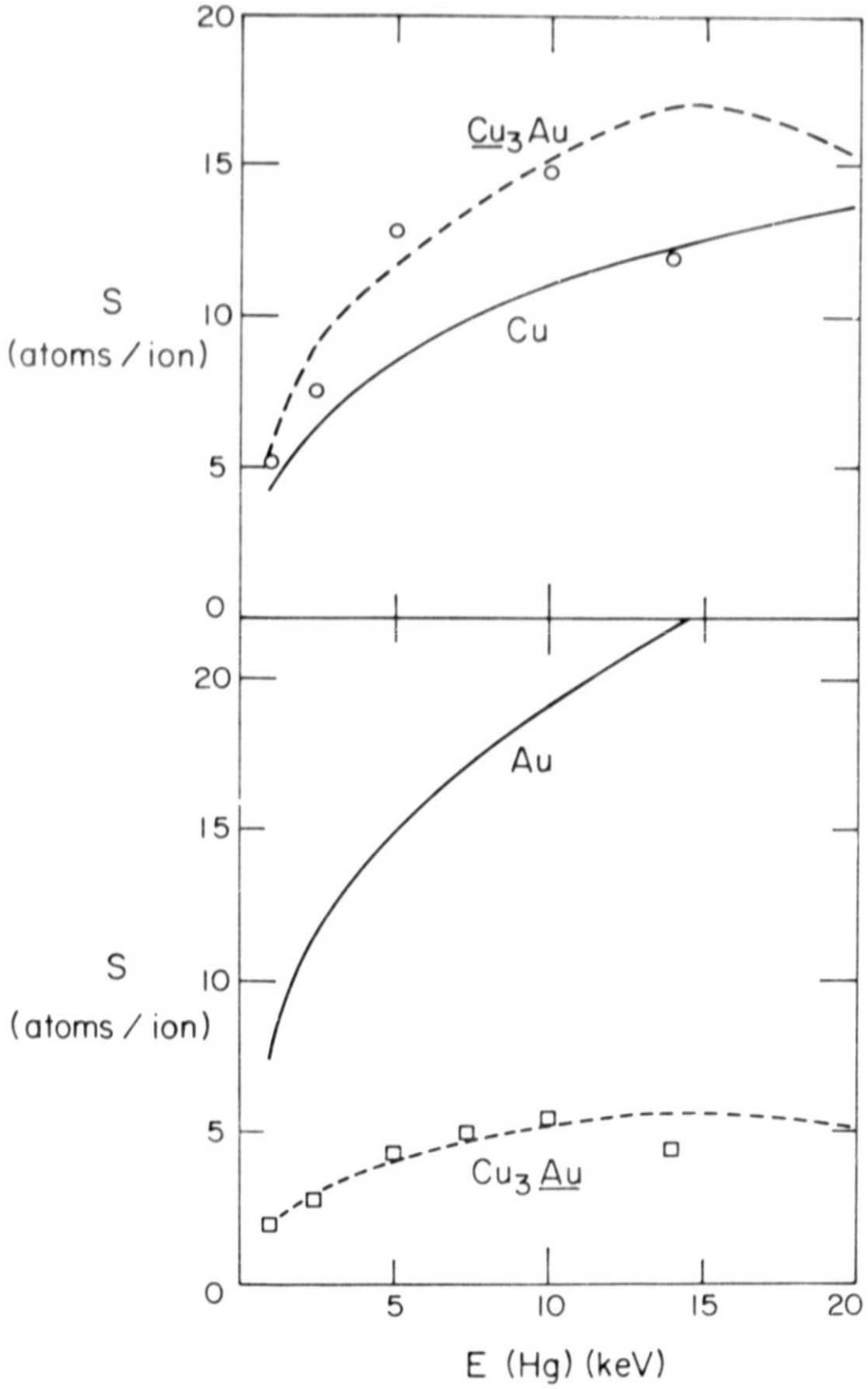
20
15
10
5
0
S
(atoms / ion)
Cu3Au
Cu
20
15
10
5
0
S
(atoms / ion)
Au
Cu3Au
5
10
15
20
E (Hg) (keV)

Fig. 2