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Anomalous coverage dependence of secondary-ion emission from overlayers

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We have observed an anomalous coverage dependence of sputtered Cs⁺ and Li⁺ yields from Cs and Li overlayers on Si(111) surfaces. The ion yield reaches a maximum and decreases at higher coverages even when the coverage is still less than a monolayer. We found that this phenomenon is directly related to the effect of the work function on the ionization probability.

In this study of secondary-ion emission during ion beam sputtering from adsorbed atomic layers on surfaces, it is not infrequently found that the atomic ion emission is not very linear with the concentration of adsorbates on the surface. This often happens when the amount of adsorbate exceeds one monolayer (ML) or there is a change in the surface chemistry at certain coverages during chemisorption.¹⁻³ Recently Prigge and Bauer⁴ reported that for the case of metallic (Pd, Cu, Y) overlayers on W(110) surfaces, the Pd⁺ and Cu⁺ yields are quite linear with the overlayer concentration at least up to 1 ML coverage. However, the concentration dependence of the Y⁺ yield is anomalous. The Y⁺ increases with the coverage initially but reaches a sharp maximum at coverage $\Theta=0.05$ ML, then a minimum at $\Theta=0.5$ ML, followed by an increase up to $\Theta=1$ ML. This is surprising since no big change in the Y-W bond with coverage is expected. Lately Lamartine, Czarnecki, and Haas⁵ also observed a similar phenomenon for the sputtered O⁻ yield during oxygen adsorption on a Ba-covered W surface. In this paper, we attempt to identify the cause of the coverage anomaly.

It is important to note that, in both experiments, the adsorbates Y and O change the work function Φ of the surfaces. This point is also mentioned in Refs. 4 and 5. In general, the sputtered secondary-ion yield S^+ is given by

$$S^+ = \beta S^0 \Theta P^+ I_p, \quad (1)$$

where β is the instrument sensitivity factor, S^0 is the sputtering cross section, P^+ is the ionization probability, and I_p is the primary-ion beam current. β , S^0 , and P^+ can all be functions of the emission energy and angle. If we assume that the anomaly in the coverage dependence is a purely work-function effect, then

$$dS^+/d\Theta = \beta S^0 I_p P^+ [1 + (\Theta/P^+)(dP^+/d\Theta)] .$$

For overlayers of electropositive elements, $d\Phi/d\Theta$ is usually negative. Hence if $dP^+/d\Phi$ is large, there would be a critical coverage Θ_c at which S^+ reaches a local maximum. At this point, the increase in the sputtering yield due to the increase in coverage is compensated by a decrease in the

ionization probability. Recently it has been observed⁶ that the work-function dependence of positive ionization of sputtered atoms can be divided into two regions. When the work function Φ of the surface is larger than the ionization potential I of the sputtered atom, the ionization probability P^+ is independent of Φ and is equal to unity according to the electron tunneling model.^{6,7} When $\Phi < I$, P^+ tends to be an exponential function of Φ for small range of Φ .

$$P^+ \propto \exp[(\Phi - I)/c\nu_{\perp}] , \quad (2)$$

where ν_{\perp} is the normal component of the sputtered atom emission velocity, and c is a constant characteristic of the surface-atom interaction. An electron tunneling model has been proposed to explain this behavior.⁶ According to this model, P^+ is given with sufficient accuracy by

$$P^+ = \exp[-2\Delta(z_c)/\gamma\nu_{\perp}] , \quad (3)$$

where z_c is the distance from the surface at which the atomic level crosses the Fermi level and $\Delta(z_c)$ is the half-width of the atomic level at z_c . γ is the inverse decay length of $\Delta(z)$. In this experiment we try to determine the relation between the anomalous coverage dependence and these established dependences of P^+ on Φ .

We have selected for study the sputtering of Cs overlayers on Si(111) surfaces for the following reasons. Firstly, $I(\text{Cs})$ is 3.9 eV while Φ of Si(111) is 4.6 eV (Ref. 8) and the maximum $\Delta\Phi$ achievable with a Cs overlayer is about -3.2 eV. Hence both $\Phi > I$ and $\Phi < I$ regions can be covered. Secondly, the adsorption of Cs on Si(111) is limited to a single layer of about 2×10^{14} atoms/cm² (Ref. 9) at room temperature, thus avoiding complicated multilayer conditions. Thirdly, the work-function dependence of sputtered Cs⁺ yield has been studied before, using a Li dipole layer to induce $\Delta\Phi$.⁶ The experimental setup has been described before.⁶ Briefly, the experiment was performed in an ultrahigh vacuum chamber with about 2×10^{-10} Torr base pressure and which is equipped with *in situ* low-energy electron diffraction and Auger analyzer. Cs was deposited on a clean 10- Ω -cm *n*-type Si(111)-(7 \times 7) surface by thermal evaporation from a thoroughly outgassed Cs getter.¹⁰

The 47-eV Cs Auger peak was used to monitor the coverage. $\Delta\Phi$ was measured by an electron-beam-retarding field technique. A differentially pumped ion gun provided a 500-eV, 1-nA, 3-mm-diam Ne^+ beam for sputtering in the low-damage static-mode condition. The secondary ions were detected at right angles to the incident Ne^+ beam direction and at about 25° with the normal to the sample surface. The secondary ions were first energy analyzed with a 0.5-eV band pass energy filter with a weak (~ 2 eV) extraction field and then detected by a quadrupole mass spectrometer.

The coverage dependence anomaly is observed clearly with the Cs overlayer. Figure 1 shows the Cs coverage dependence of the sputtered Cs^+ yield at two emission energies, 6.2 eV (3×10^5 cm/s) and 33.8 eV (7×10^5 cm/s). The highest Cs coverage used corresponds to the maximum allowable coverage at room temperature. Using the coverage calibration from Ref. 9, the Cs^+ yields reach their maxima at about 6×10^{13} atoms/cm² with a $\Delta\Phi$ of about -2 eV. The coverage dependence beyond these maxima also displays strong emission energy dependence. The decrease in the Cs^+ yield after the maximum is significantly faster at low emission velocities. Recently Wittmaack¹¹ observed that the time dependence of the sputtered Cs^+ yield during Cs^+ bombardment of Si also displays a maximum. His ob-

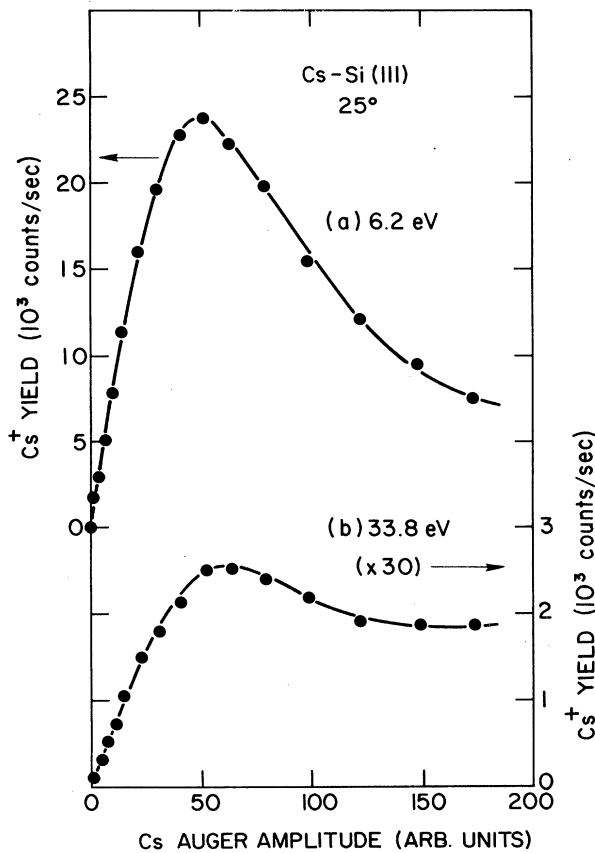


FIG. 1. The sputtered Cs^+ yield as a function of Cs coverage as expressed by the Cs Auger signal at two emission energies (a) 6.2 eV and (b) 33.8 eV. According to the coverage determination in Ref. 9, the maximum Cs Auger signal corresponds to 2×10^{14} atoms/cm².

servation may have a similar physical origin.

The relative ionization probability P^+ can be obtained by normalizing the Cs^+ yield to unit Cs coverage. As shown in Fig. 2, the ionization probability is initially practically independent of $\Delta\Phi$ in the range from 0 to -1 eV. It is followed by the gradual onset of a rapid decrease in P^+ as the work function is being lowered further. These data are very similar to the result obtained for Cs^+ when $\Delta\Phi$ is induced independently with a Li dipole layer.⁶ The initial independence of P^+ on $\Delta\Phi$ corresponds to the $\Phi > I$ region together with a delay of the onset of strong neutralization by about 0.3 eV as observed in Ref. 6. According to the electron tunneling model, the delayed onset results from the fact that z_c in Eq. (3) has to be small enough (i.e., $I - \Phi$ large enough) to have effective electron tunneling. For $\Delta\Phi < -1$ eV, P^+ starts to decrease with the decrease of Φ and tends to approach the exponential dependence on Φ at the low-work-function region. The more rapid decrease in P^+ with Φ at the lower emission energy is consistent with the dependence on the normal component of the escape velocity v_{\perp} . A quantitative comparison with Eq. (3) would require a good knowledge of $\Delta(z)$ which is not available at present.

The sputtering of Li^+ from Li overlayers on Si(111) was also studied. The ionization potential of Li is 5.4 eV, which is larger than Φ of Si(111) and we do not expect a Φ -independent region for P^+ of Li. Still the anomalous Li^+ yield maximum is observed as shown in Fig. 3(a) at $\Delta\Phi \sim -1.75$ eV. The change in Φ is limited to about 2 eV in the case of the Li overlayer. Unfortunately, Auger analysis cannot be used to monitor the Li coverage. If we assume that the ratio of the sputtering cross sections S^0 at different emission energies remains constant as the Li coverage changes, we can study the Φ dependence of the ioni-

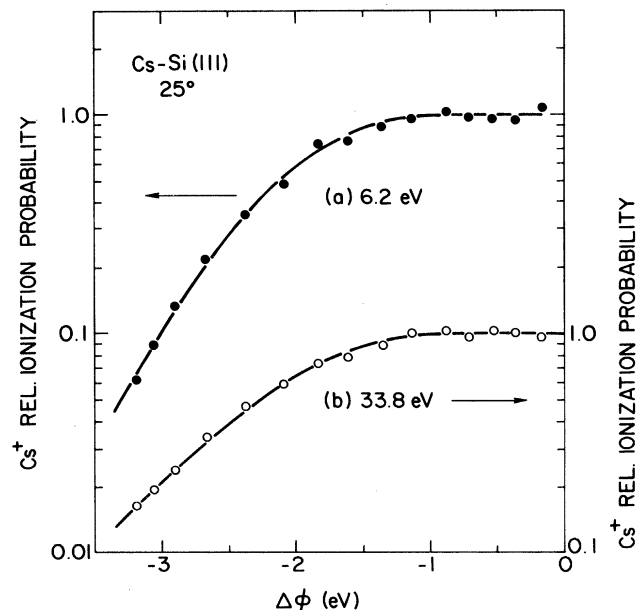


FIG. 2. The Cs relative ionization probability as a function of work-function change $\Delta\Phi$ at two emission energies (a) 6.2 eV and (b) 33.8 eV. The average of the five data points between $\Delta\Phi = 0$ and -1 is normalized to unity.

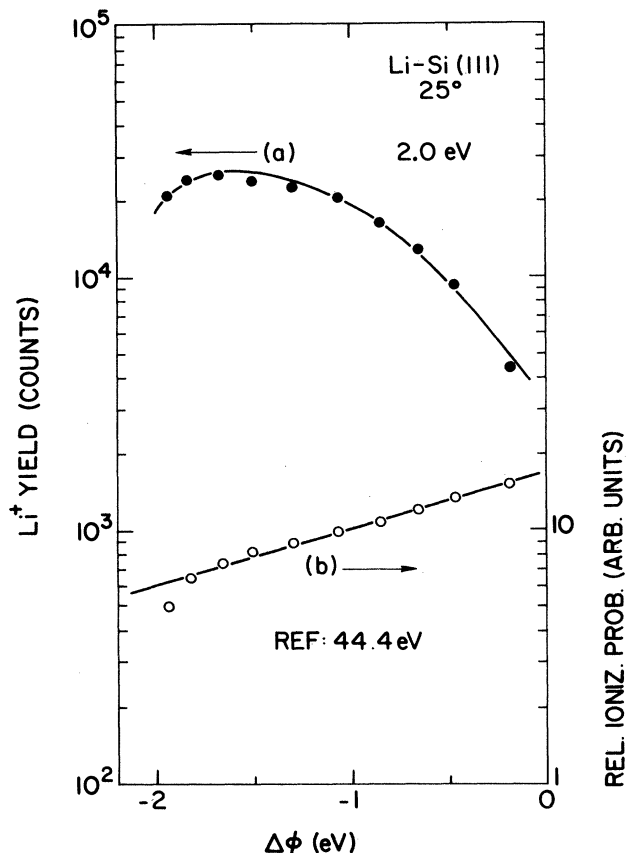


FIG. 3. (a) The Li^+ yield sputtered from a Li overlayer on Si(111) as a function of the work function change $\Delta\Phi$. (b) The relative ionization probability of the sputtered Li atoms emitted with 2 eV normalized to that emitted with 44.4 eV as a function of work function change $\Delta\Phi$. Notice the exponential dependence on $\Delta\Phi$.

zation probability by taking the ratio of the Li^+ yields at different emission energies (velocities) but at the same $\Delta\Phi$ to eliminate the factor Φ in Eq. (1). Figure 3(b) shows the $\Delta\Phi$ dependence of the ratio between the Li^+ yields at 2.0 eV (7.4×10^5 cm/s) and at 44.4 eV (3.5×10^6 cm/s) follows reasonably an exponential dependence on $\Delta\Phi$ as expected from Eq. (2). In this case, where $I > \Phi$ throughout the whole range of Φ no Φ -independent region is observed.

The anomaly observed in the sputtering of ionized yttrium by Prigge and Bauer⁴ can also be explained by Eq. (2). Since I of yttrium is 6.38 eV while Φ of W(110) is about 5.25 eV,⁸ I is larger than Φ over the whole coverage range of Y on W(110). By extracting the data from Fig. 6 in Ref. 4, we found that Y^+/Θ (ion/ n in Ref. 4) which is proportional to P^+ depends exponentially on $\Delta\Phi$ up to the work-

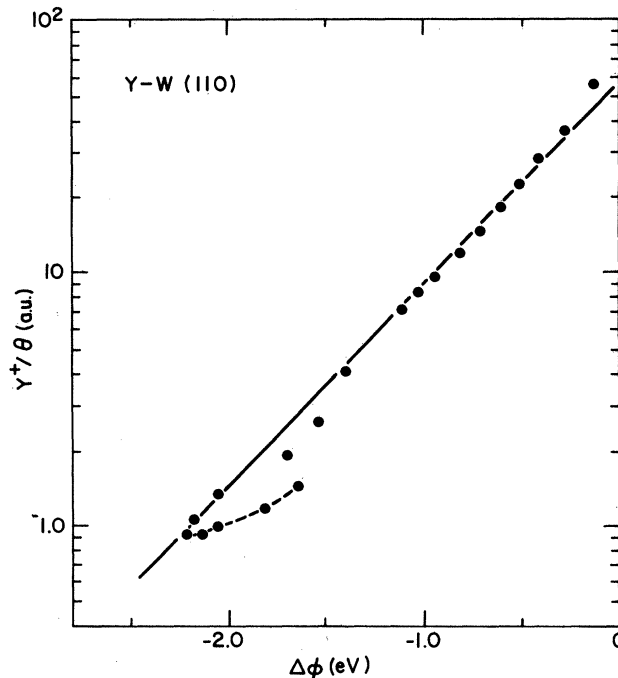


FIG. 4. The Y^+ secondary-ion yield, normalized to unity Y coverage as a function of the work-function change $\Delta\Phi$. Data are extracted from Fig. 6 in Ref. 4. Notice the exponential dependence on $\Delta\Phi$ for the low-coverage data before reaching the work-function minimum. The high-coverage data points beyond the Φ minimum are connected by the dashed line.

function minimum, in good agreement with Eq. (2). The data deviate somewhat from the exponential dependence at coverages beyond the Φ minimum (see Fig. 4). No explanation is available yet for this complication at higher coverages.

To summarize, we have shown that the anomalous coverage dependence of the secondary-ion yields sputtered from metal overlayers on solid surfaces is directly related to the effect of the work function on the ionization probability P^+ in all the cases examined. This study also shows that P^+ of a sputtered atom would be affected by the work-function change induced by the same atomic species on the surface, even though there may not be any major change in the bonding with coverage. This anomalous coverage dependence of the secondary-ion yield is another demonstration of the importance of work function on the ionization probability of sputtered atoms.

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¹M. L. Yu, Surf. Sci. **71**, 121 (1978).

²T. Fleisch, N. Winograd, and W. N. Delgass, Surf. Sci. **78**, 141 (1978).

³A. Benninghoven, H. Bispinck, O. Ganschow, and L. Wiedmann, Appl. Phys. Lett. **31**, 341 (1977).

⁴S. Prigge and E. Bauer, Adv. Mass Spectrom. **8A**, 543 (1980).

⁵B. C. Lamartine, J. V. Czarnecki, and T. W. Haas, J. Vac. Sci. Technol. A **1**, 1034 (1983).

⁶M. L. Yu and N. D. Lang, Phys. Rev. Lett. **50**, 127 (1983).

⁷N. D. Lang, Phys. Rev. B **27**, 2019 (1983).

⁸CRC Handbook for Chemistry and Physics, 63rd ed. (CRC, Boca Raton, FL, 1982).

⁹P. Wagner, K. Müller, and K. Heinz, Surf. Sci. **68**, 189 (1977).

¹⁰SAES Getters, Colorado Springs, CO 80906.

¹¹K. Wittmaack, Surf. Sci. **126**, 573 (1983).