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A Comment on the Effect of Cs on Photon and Secondary Ion Emission During Sputtering*

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Abstract

The effect of Cs on photon and negative ion emission was discussed for the situations where the sputtered atom interacts either very weakly or very strongly with the target surface. The experimental data seem to favor the strong interaction case.

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In the past few years there were two experiments reported in detail on the effect of adsorbed Cs on the photon[1] and negative secondary ion[2] yields during ion bombardment of solid surfaces. In both cases the adsorbed Cs was used to lower the work function of the target surface. Hopefully, from the work-function dependences of these inelastic processes, we can improve our understanding of the electronic transitions involved.

In a sophisticated experiment by Thomas et al,[1] it was demonstrated that Cs adsorption did *not* enhance photon emission from clean Cu and Al surfaces. It was proposed that the Cs dipole layer caused a relative displacement of the energy levels of the sputtered atoms with respect to the Fermi level. With the right amount of Cs, the excitation level should be shifted well below the Fermi level. This blocked the resonance tunneling channel and the excited atom could only decay by photon emission. Since experimentally, no enhancement in optical emission was observed, the result casted doubt on the validity of the resonant electron tunneling model in photon emission.

In another recent experiment,[2] the effect of Cs on negative ion formation was investigated. It was found that Cs adsorption enhanced the negative ion yields by few orders of magnitude. It was suggested that resonant electron tunneling was the mechanism for the formation of the negative ions. In this tunneling model, the energy level associated with the negative ion was assumed not to change much with respect to the Fermi level of the target. The Cs overlayer only lowered the tunnel barrier so that the probability to fill the negative ion energy level was enhanced. So there is an apparent disagreement between the two interpretations. This paper is an attempt to clarify the situation.

The effect of Cs is a surface phenomenon. The interaction between a sputtered atom and the surface can be represented by an energy diagram. It is convenient to use the vacuum level at infinity as the energy reference for the various energy diagrams. As shown in Fig. 1, the Fermi level of the metal substrate lies below the vacuum level at infinity by an amount equal to the work function ϕ_o of the pure metal.[3] If Cs is deposited onto the right hand side of the sample to lower the work function by $\Delta\phi$, the "local" vacuum level on the right will be lowered by this same amount. As a consequence, it takes less energy ($\phi_o - \Delta\phi$) to remove an electron from the inside of the metal sample. With this choice of energy reference, the Fermi level of the metal is fixed in the diagram with the vacuum level at infinity, while the "local" vacuum level is allowed to move. An interesting observation is since the local vacuum level on the right side of the metal is lower than that at infinity, there is an electric field induced between the cesiated metal surface and infinity. This field is so weak that it can be neglected under ordinary circumstances. However, if the vacuum level at infinity is replaced by the vacuum level of a close by reference metal, the induced electric field provides the way to measure the work function difference, for example, by Kelvin probe.

When the sputtered particle is sufficiently far away from the target surface (region 1) so that the chemical interaction between the two is very small, the situation assumed in ref. 1 applies. This is illustrated in Fig. 2. Consider an atom outside the target metal surface. The vacuum level of the pure metal has to match the vacuum level of the isolated atom. So when the work function and hence the "local" vacuum level of the metal is shifted by an amount $\Delta\phi$ with respect

to the Fermi level, the energy difference between the atomic level and the Fermi level is decreased by the same amount $\Delta\phi$. The tunnel barrier height, however, remains the same. The conclusions drawn in ref. 1 was based on this model.

On the other hand, when the atom is close to the surface, there is a strong chemical interaction between the atom and the target (region 2). The chemical bond determines the position of the valence electron level with respect to the Fermi level. Changes in the work function only indirectly affect the energy levels. This has been demonstrated by photoemission in many cases. For example, the hydrogen induced photoelectron peaks of the H-W(100) chemisorption system[4] did not shift in energy with respect to the Fermi level when the hydrogen coverage was changed. On the other hand the work function increased linearly with coverage. Saturation coverage was found to give a $\Delta\phi$ of 0.85 eV. Smith et al[5] also looked at the Cs levels during Cs deposition on W(100). The Cs $5p_{3/2}$ level only shifted by 1.0 eV between very small Cs coverage and the Cs coverage for minimum work function with $\Delta\phi \simeq -2.6$ eV. So to the first order approximation, the work function ϕ only determines the surface potential barrier (Fig. 3). Thus as an atom moves away from the surface, there is a gradual transition from region 2 where the positions of atomic levels are determined by the chemical bonding and not by ϕ, to region 1 where the levels follow exactly the changes in ϕ.

In ref. 1 the excited particles were assumed to be in region 1. However, there is some difficulty in trying to explain the negative ion results if we assume the same physical picture. In ref. 2, three negative ion species M^-, H^- and O^-, all originating from a cesiated

Mo(100) surface were investigated. The electron affinities of these ions are 1.18, 0.77 and 1.46 eV, respectively, but the minimum work function of a cesiated Mo surface is 1.54 eV. So in region 1, the negative ion levels are all above the Fermi level and the electrons would not be able to tunnel out from the Mo surface to form negative ions. In the experiment, Cs enhancement of negative ion yields was observed even when the work function was still close to 4 eV. One possible explanation is the electronic transitions actually occurred very close to the surface so that the image potential $e^2/4r$ could lower the negative ion level below the Fermi level of Mo. At this distance, the region 1 situation would not be applicable anymore. In ref. 2, the region 2 approximation was assumed. It was posulated that there was a finite probability to convert the escaping atoms into negative ions through resonant electron tunneling. The tunneling probability p is related to the tunnel barrier height V_o and barrier width a by[2]

$$p \propto \exp\left[-2\left(\frac{2m}{\hbar^2}\right)^{1/2} (V_o-E)^{1/2} a\right] \qquad (1)$$

where E is the energy of the electron. It was further assumed that the Cs overlayer changes the barrier height V_o by $\Delta\phi$ so that

$$V_o-E = V_1 + \Delta\phi \ , \qquad (2)$$

where V_1 is the initial barrier height when there was no Cs. This gives a functional relationship between p and $\Delta\phi$. The model fitted the negative ion enhancement data very well. Estimates of V_1 and a from the data have very reasonable physical values.[2]

It is of interest to see the effect of Cs on photon emission in region 2. The image potential would raise the excited level of the neutral atom by $e^2/4r$ approximately, placing it above the Fermi level of the metal target. In fact, the excitation levels of the atoms of the target all lie above the Fermi level. If the atoms are excited during sputtering, deexcitation can occur through resonant electron tunneling back to the metal. The Cs overlayer lowers the potential barrier, making the deexcitation process even more probable. So a lower work function would not enhance the photon yield. This model thus arrives at a conclusion which is different from that in ref. 1. It is, however, consistent with the experimental observation. So if the region 2 interaction is taken into account for photon emission, the experimental result in ref. 1 could not conclusively rule out the electron tunneling mechanism.

The actual state of an escaping particle is obviously far more complicated than the approximations taken in region 1 or region 2. It should be a spatially dependent intermediate state between the two extremes. An investigation on the gradual evolution of the particle-surface interaction along the trajectory of the moving particle would be very useful.

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FIGURE CAPTIONS

Fig. 1 Energy diagram of a metal target with Cs on the right hand side to lower the local work function. The vacuum level at infinity and the Fermi level of the metal are fixed in this diagram while the local vacuum level changes with the work function.

Fig. 2 Energy diagram of an atom in region 1. The atomic level shifts with work function change $\Delta\phi$ while the potential barrier A for tunneling remains unchanged.

Fig. 3 Energy diagram of an adsorbed atom in region 2. The atomic level is fixed by the chemical bond. The potential barrier for tunneling changes with $\Delta\phi$.

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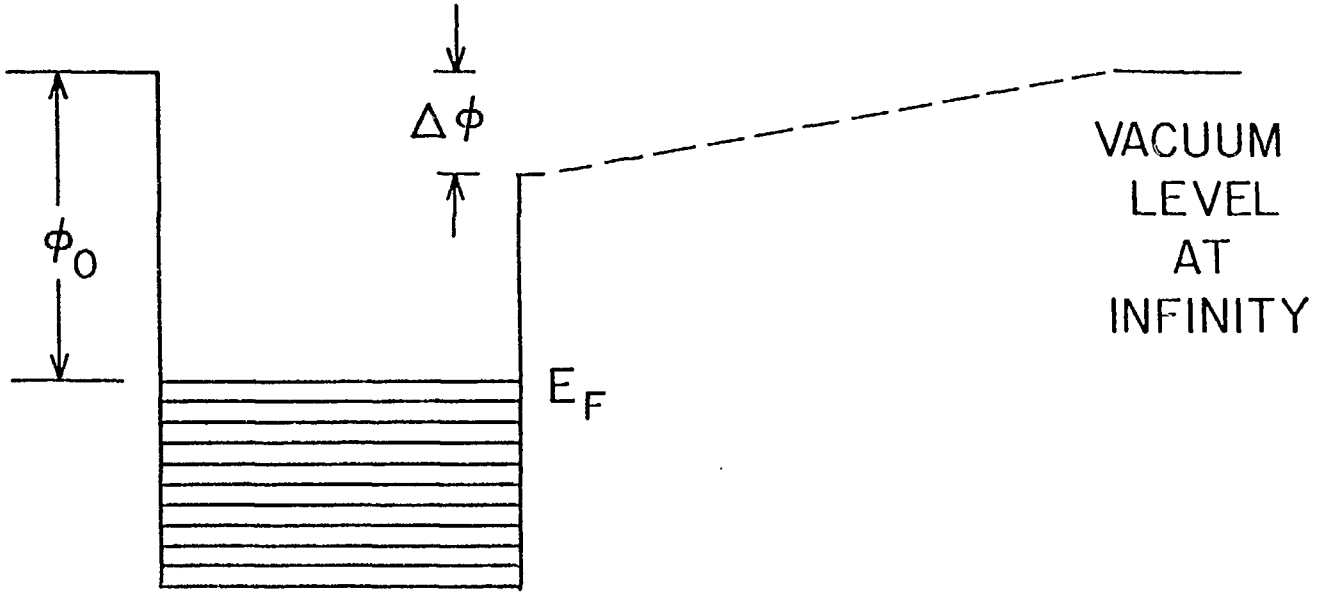

Fig. 1

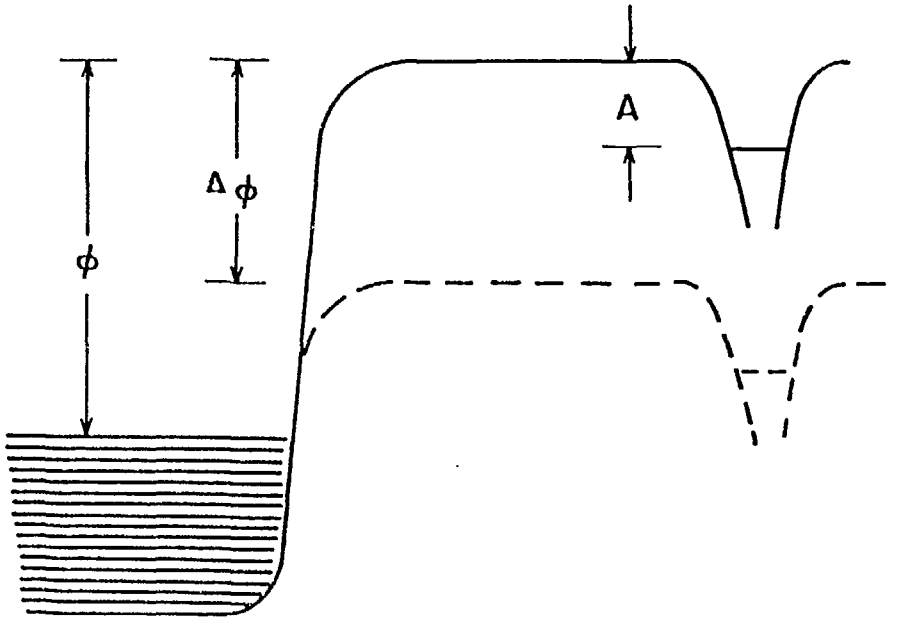

Fig. 2

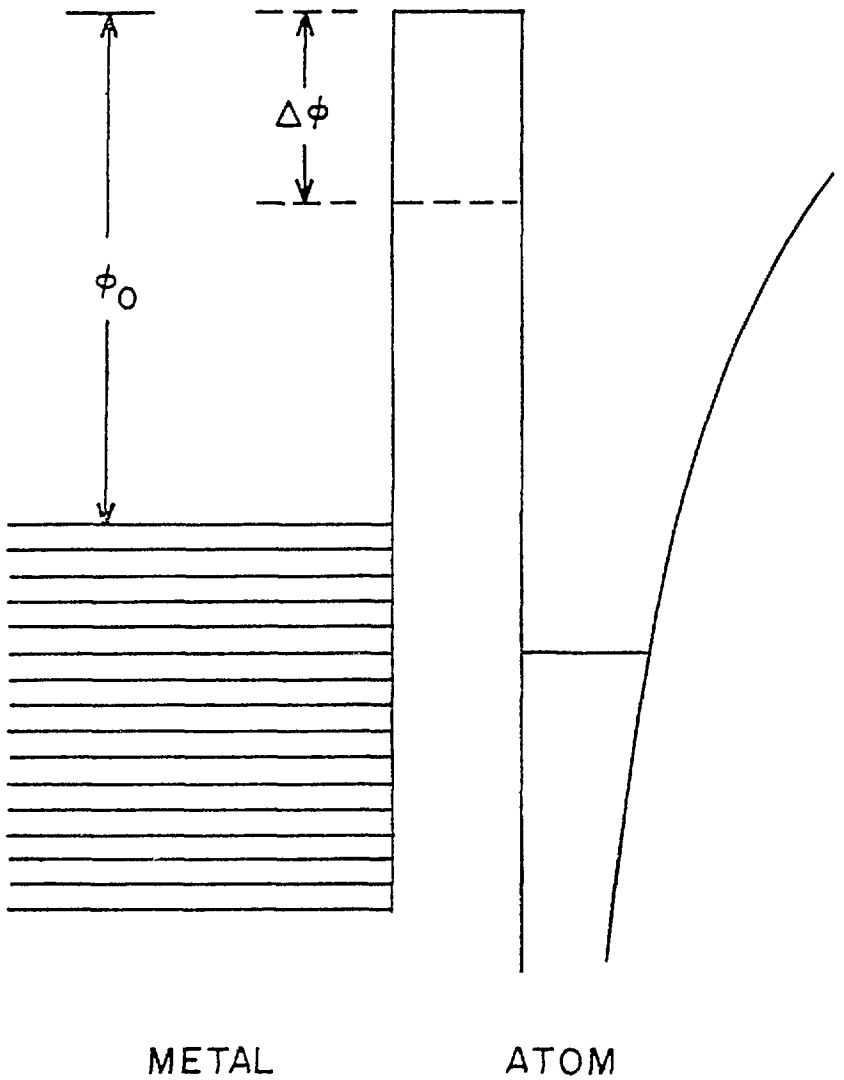

Fig. 3