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LETTER TO THE EDITOR

Plasmon production in the x-ray photoelectron spectra of Ar and K implanted in Al and Si

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Abstract. We have investigated plasmon production in the XPS spectra of Ar and K implanted in Al and Si. We have studied these systems to obtain further information on intrinsic and extrinsic processes. We have found differences between the spectra of Ar and K for both substrates. The results show that in these systems the intrinsic contribution to plasmon production is greater than the extrinsic one. The results also show that the intrinsic process for K is very weak; we attribute this to the fact that the interaction between the K photohole and the plasmon field is screened by the 4s electron.

XPS (x-ray photoelectron spectroscopy) spectra of solids usually show distinctive satellites. They correspond to excited final states of the solid in the photoemission process. In simple metals, the excitations can be due to electron-hole pair creation (single-particle excitation) or to plasmon creation (collective excitation). Extrinsic plasmons are excited by fast photoelectrons on their way through the solid towards the surface. On the other hand, intrinsic plasmons are excited by the sudden change of potential due to the creation of the photohole.

XPS spectra of pure simple metals have been studied to distinguish the relative importance of intrinsic and extrinsic contributions to plasmon production, as detailed in [1–6]. This literature suggests that extrinsic plasmon production contributes 60-90% of the observed plasmons in XPS of simple metals. Other authors have investigated plasmon production in inhomogeneous systems [7–9]. Plasmon production in XPS has been the subject of a number of excellent theoretical treatments [10–12]. The interference terms between intrinsic and extrinsic processes have also been studied [2, 13].

We have studied plasmon production in the XPS spectra of Ar and K implanted in Al and Si, with the purpose of obtaining further information on intrinsic and extrinsic processes. We have found significant differences between the spectra of Ar and K for both substrates. These results show that in these systems the intrinsic component yields the main contribution to plasmon production. The results also show that the intrinsic component for K is very weak; we suggest that this is due to the interaction between the K photohole and the plasmon field being smaller because of screening by the 4s electron.

The experiments were carried out using surface spectroscopy equipment described earlier [14]. The base pressure in the UHV chamber was in the low 10^{-10} Torr range. The substrates were high-purity polycrystalline Al and amorphous Si cleaned by sputtering with low-energy Ar ions. Cleaning was continued until oxygen contamination was below



the detection limits of our AES (Auger electron spectroscopy) system. Argon ions were produced in a glow discharge chamber; the implantation energy was 2 keV and the ion current density was 40 μ A cm⁻². Potassium ions were obtained by thermal evaporation from a thoroughly outgassed glassy source; the implantation energy was 2 keV and the ion current density was 20 μ A cm⁻². The concentration of Ar and K implanted in the substrates was estimated using quantitative AES; it was approximately 5%. The spectra were obtained using Al K α photons as the excitation source. The hemispherical electrostatic analyser was operated with a constant energy resolution of 1 eV. The energy scales have not been corrected to account for the spectrometer work function.

An important experimental fact should be stressed: oxygen contamination of the surface should be avoided because oxygen induces surface segregation of K and it forms clusters of K oxide. To this end, the absence of oxygen contamination was always checked after each data acquisition process. Migration and nucleation effects could be neglected because the implanted-atom concentration and measuring time were small.

Figure 1(a) shows the XPS spectrum of the 2p level of Ar implanted in Al. A strong satellite due to the excitation of Al bulk plasmons is clearly seen in this spectrum. Figure 1(b) shows the XPS spectrum of the 2p level of K implanted in Al. The plasmon loss satellite has much less intensity in this spectrum, being almost lost in the background. The weakness of the plasmon satellite for K implanted in Al shows that neither intrinsic nor extrinsic effects are important in this system.

One should remark that in these experiments Ar and K have been implanted into Al at the same energy. Furthermore, they have similar mass. Therefore, the concentration-depth distributions should be nearly equal and the photoelectrons should be generated in similar conditions. As is well known, the extrinsic effects depend only upon the photoelectron kinetic energy and on the electronic structure of the traversed material. Therefore, the weakness of the extrinsic contribution for K in Al indicates that this process should not be important for Ar in Al either, because the photoelectrons in the two cases have almost the same kinetic energy.

Then plasmon excitation for Ar implanted in Al is mostly due to intrinsic effects. Why are the intrinsic processes in Ar more intense than in K? We think that a key to the answer can be obtained from the work of Bradshaw and co-workers [9]. The K 4s electron surrounds the neighbourhood of the ion core, so as to assure charge neutrality, and its energy lies at the Fermi level. Upon photoionisation, this electron relaxes to screen the photohole, so it is localised onto the ion core and its energy is slightly lowered. The net



Figure 2. XPS spectra of the 2p peak of (a) Ar and (b) K, implanted in Si.

effect is to screen the long-range part of the photohole potential, reducing the coupling with the plasmon field. Hence, the intrinsic contribution should be diminished.

To rule out the probability of unforeseen effects that might lead to a particular cancellation in the K-Al case, we have also studied the plasmon production in the XPs spectra of Ar and K implanted in Si. The spectrum of Ar implanted in Si in the Ar 2p region is shown in figure 2(a); a strong satellite due to the excitation of Si bulk plasmons is clearly seen. Figure 2(b) shows the corresponding spectrum of K implanted in Si. As in the case of figure 1(b), in this spectrum the satellite also has much less intensity. Hence, the characteristics of plasmon production for Ar and K implanted in Si are similar to those observed for the same impurities implanted in Al.

At room temperature, Ar is not stable on top of the surface. On the other hand, K can bind to solid surfaces exchanging charge with the substrate. Thus, one could imagine that a large fraction of K atoms may be on top of the surface, which would lead to incorrect analysis. But the K atoms are implanted with a kinetic energy of 2 keV, so in addition we have a sputtering effect. Therefore, the fraction of K atoms on top of the surface should be negligibly small, because upon sputtering these atoms are more easily removed than those implanted deep in the bulk. Then, although there might be a slight difference in concentration of Ar and K on top of the surface, this is not large enough to explain the differences in the spectra. One should also remark that both experimental measurements and Monte Carlo simulations indicate that the projected range of 2 keV Ar and K ions in Al is approximately 25 Å and their distribution width is about 30 Å; ([15]; see also [16]), and that for 1 keV photoelectrons in Al the escape depth is approximately 20 Å ([17]; see also [18]). Hence, our XPS experiment samples not only the surface itself but also a depth of four to five atomic layers, where the Ar and K atoms are equally distributed.

The differences between the spectra of Ar and K cannot be explained in terms of extrinsic processes alone. In fact, the experimental results for K indicate that the extrinsic processes do not yield the main contribution to plasmon creation. This result is rather surprising because the extrinsic contribution is clearly seen in EELS spectra [6] and extrinsic plasmon production is the largest source of inelastic scattering for electrons in the energy range studied [19]. The lack of an extrinsic process in these cases may arise from the implantation depth of the impurities (25 Å) [15, 16] being smaller than the calculated plasmon inelastic mean free path for 1 keV electrons in Al (33 Å) [19].

The analysis of the experimental results indicates that the intrinsic component for 1 keV photoelectrons, from implanted impurities in Al and Si, is larger than the extrinsic

one. This conclusion is in agreement with the predictions of the theory [11-12]. However, one should notice that a different conclusion was obtained for homogeneous simple metals by previous authors [1-6]. We cannot explain the origin of this discrepancy at the moment, but it may be related to the reduced extrinsic contribution discussed above.

We cannot disregard the possibility that the suppression of the intrinsic component in the spectra of K may be partly due to interference effects. Fuggle and co-workers have found a reduction in the intrinsic component of 20% for 1 keV photoelectrons in simple metals [13]. However, this reduction alone is not large enough to explain the weakness of the plasmon losses for K and, in addition, it would not give rise to the difference between the K and Ar spectra. Therefore, we propose another explanation for this effect, in terms of the screening provided by the K 4s electron and the ensuing reduction of the coupling between the photohole and the plasmon field.

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