Observation of Hollow Atoms or Ions above Insulator and Metal Surfaces

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We present some experimental results which demonstrate that hollow atoms (ions) can be formed above insulator surfaces, and show for the first time dramatic differences in the interactions of a given ion with a metal and a semiconductor (insulator) surface, leading to the formation of different hollow atoms (ions). These results are tentatively explained in considering the localized (valence) or delocalized (conduction) character of the captured electrons and the backscattering of the ions above insulators. [S0031-9007(96)00951-9]

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When a slow highly charged ion approaches a metal surface, a large number of electrons can be captured into highly excited states of the ion leading to the formation of hollow atoms. In this case the metal surface constitutes an infinite reservoir of weakly bound conduction electrons, and the ion may be quasi-instantaneously neutralized at large distances from the surface. These "outside the surface" hollow atoms are, however, extremely difficult to observe and study because these excited ions have only a very short lifetime before hitting the surface where they are peeled off [1]. The x-ray and Auger lines emitted by the ions then originate mainly from the hollow atoms created below the surface [2,3], and only a very small part comes from outside the surface.

Although their detailed decay processes cannot be accurately analyzed, the formation of these "outside" hollow atoms has been observed [3–9] by looking at the *KLL* (or *LMM*) Auger lines and the *K* x rays emitted in flight by the ion at grazing incidence (increase of the time spent by the ion outside). This approach was first made, for metals, by Meyer *et al.* [3] using Auger spectroscopy with N^{6+} ions, and by Schulz *et al.* [5] using x-ray spectroscopy with Ar^{17+} ions on Ge targets. This method is now a classical tool for studying the formation of hollow atoms above a surface [3–7]. The well accepted model for this interaction is that outside the surface many electrons are captured in Rydberg states through a resonant neutralization process. These highly excited states then decay to the ground state through a long series of Auger transitions involving many intermediate states. The characteristic of this cascade, as described in Ref. [7], is that the electrons move by successive waves along these intermediate states, leading to the so called triangular population which, after a certain time, ends up with the arrival of a first electron on the *L* shell. In such configurations with only one *L* electron, the transition probabilities for a new filling of the *L* shell and the filling of the *K* shell through the emission of, e.g., a $K\alpha$ line are comparable (or only slightly larger). Then one must observe the characteristic x-ray spectra of atoms having only one (or two) *L* electron. Below or at the surface, the capture process, which takes place at much closer distances, populates the *M* and *N* shells [2]. There are thus two different kinds of hollow atoms: those formed outside the surface populating the Rydberg states and those formed below or at surface filling the *M* and *N* shells.

In the "below surface" hollow atoms, the *M* (*N*) electrons very quickly fill the *L* shell (there is just one step and the *LMM* Auger rates are very large). The $K\alpha$ decay then takes place at any time of the *L* shell filling, and one observes the $K\alpha$ transition in the presence of any number *x* of *L* electrons ($1 < x < 8$) [2,10]. With the energies of the satellite lines corresponding to each state of population of the *L* shell being distant in energy by 25 eV, one observes at high resolution a characteristic spectrum of below surface hollow atoms made of 8 lines, well separated at high resolution, having roughly the same intensity. At grazing incidence the fraction of outside decay increases, and the relative intensity of the KL^1 or KL^2 lines is larger. The center of gravity of the KL^x distribution [as, e.g., observed at low resolution with Si(Li) detector] is then more peaked on the satellites having a small number of *L* electrons, i.e., located at a larger mean energy. All experiments [3–7], which demonstrated the formation of hollow atom above surfaces, have used this technique.

Most experiments to date have dealt with metal surfaces. The interaction of the slow highly charged ions with insulator targets is more difficult to study because of the static electric charges that may appear on the surfaces. The absence of a sufficient number of conduction electrons in these materials makes the formation of such outside hollow atoms or ions by highly charged ions flying over insulator surfaces also questionable. Very recently Limburg *et al.* [9] claimed that there is no formation of

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outside hollow atoms when N^{6+} ions interact with LiF surfaces.

We present in this paper two experiments that clearly establish the creation of outside hollow ions during the interaction of Ar^{17+} ions on SiO_2 (insulator) surfaces and that are compared to Limburg's results. In the first experiment we studied, at low resolution, the interaction of 20 keV/q Ar^{17+} ions at grazing incidence on SiO_2 targets and observed the signature of the formation of hollow atoms already found above metal surfaces [5–7]. In a second experiment we fully decelerated the Ar^{17+} ions and studied at high resolution their interaction at normal incidence on metal and semiconductor surfaces. We observed with ions of the same initial energy very different spectra which show that different kinds of hollow atoms or ions are formed above metals and semiconductors. We observed namely the signature of the touchdown of the ions on metals which does not appear for silicon. We tentatively explain these results by considering the backscattering of ions above insulator surfaces due to a transient and local buildup of positive charges.

In the first experiment, at grazing incidence we used a Si(Li) detector of 160 eV resolution at 6 keV, and we studied as a function of the incident angle the mean value of the energy of these eight satellites (as already done by previous authors [5–7]). In this experiment the Ar^{17+} ions were produced at a 20 keV/q energy by the 10 GHz Caprice Electron Cyclotron Resonance (ECR) source of the AIM facility in Grenoble. The mechanical alignment of the system allowed the definition of the incident angle within 0.5°. The maximum number of impinging ions was $10^5\ s^{-1}\,cm^{-2}$. Such a small number of incoming ions is favorable in two ways. First, the target surfaces remain a long time without any significant morphological degradation, meaning that each new ion finds a surface as if it had not been irradiated. Second, even in the case of an insulating target, electrostatic charging effects are negligible (in 1 μm^2, the positive charge induced by one ion has 100 s to decay before a new ion comes within the same area). We used SiO_2 clean targets prepared by high temperature oxidation of Si wafers. The thickness of the SiO_2 layer was about 870 Å (measured by nuclear analysis). The wafers were selected as cut at an angle less than 0.1° with respect to the (111) crystallographic plane, one of the faces being polished optically in order to prepare very flat surfaces.

Figure 1 displays the mean energy change of the K x-ray spectra at two different ion beam incident angles on a SiO_2 insulating target, and Fig. 2 summarizes the variation of the mean energy of the $K\alpha$ line, i.e., of the mean number of L spectator electrons at the time of the emission of the K line, as a function of the incident angle, for SiO_2 and Au targets, respectively. These curves clearly show the characteristic increase in energy of the $K\alpha$ line (i.e., the decrease of the mean number of L spectator electrons), which has been observed by many groups [5–7] and has demonstrated the formation of outside hollow atoms on

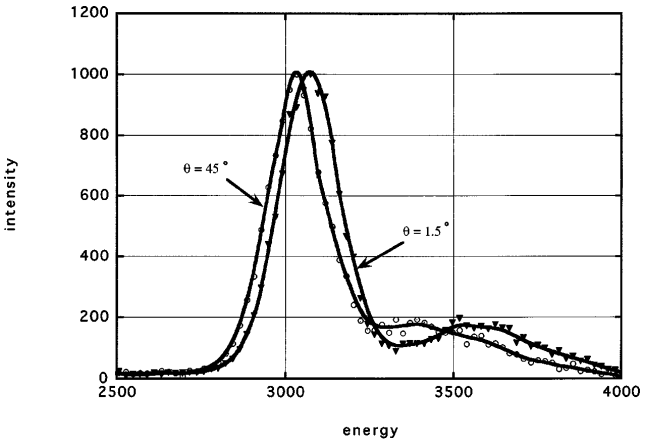

FIG. 1. K x-ray spectra observed on a SiO_2 layer at incident angles 1.5° and 45°.

metals or semiconductors. One observes in Fig. 2 the same decrease of the mean number of L electrons ($\Delta n \approx 1.5$) between the extreme angles of incidence for the insulator and the metal, i.e., the same increase of "outside decay." Outside hollow atoms are thus observed in both cases. The absolute number of L electrons is, however, at the greatest angles of incidence larger for metals than for insulators. This offset, which will be discussed in detail in another paper, is due to an increase of the electron capture in metals inside the bulk.

These results must be compared to those recently obtained by Limburg *et al.* [9] who observed no formation of hollow atoms during the interaction of N^{6+} ions above LiF (insulator) surfaces. These authors drew their conclusion in comparing, in the same kinematic conditions, the *KLL* Auger spectra emitted on Si (or metal) surfaces, where some clear signatures of the outside decay were observed (formation of KL^2 states, the KL^1 state not decaying through *KLL* Auger transitions), with those obtained above LiF surfaces (no observation of these signatures).

These results could, however, be explained in another way by considering the atomic clock property of the hollow atoms [2,7]. In $N^{6+} \rightarrow$ metal (or Si) interactions, the conduction (metal), or valence (Si) electrons, i.e., weakly bound electrons ($B \sim 6$ eV), are captured into high n states of the ion ($n = 6$–7). Owing to the relatively large number of steps for these electrons to reach the L shell (low filling rate of the L shell compared to that of the K shell), as soon as a first electron reaches the L shell the K hole filling may occur. This leads to a KL^x state distribution peaked on KL^1. Since the KL^1 state does not decay through Auger emission, only a small part of these events (the KL^2 state) is observed in Auger spectroscopy (the outside characteristic signature).

With LiF targets the electrons are more strongly bound (12 eV) and their capture must occur in lower n states ($n = 3$ or 4). The filling of the L shell is then faster, and more electrons are present in the L shell at the time of the K emission, leading to a whole Auger spectrum similar to that observed for atoms having many L electrons (below

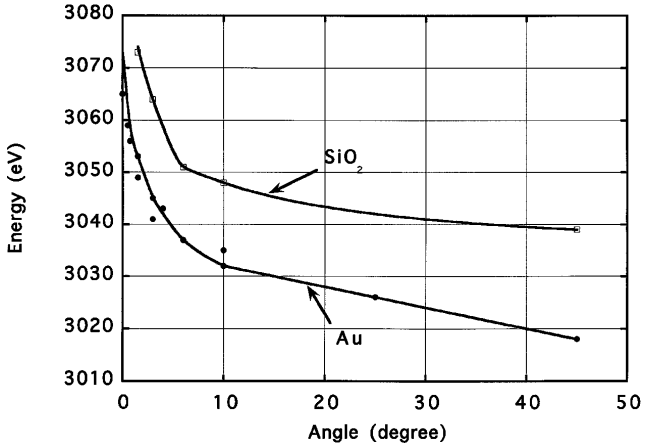

FIG. 2. Variation of the mean energy of the $K\alpha$ line as a function of incident angle for Au and SiO_2 targets.

surface interaction). Therefore, the nonobservation of significant signatures of the outside decay of hollow atoms in $N^{6+} \rightarrow LiF$ collisions may be due to the exceptionally large value of the binding energy of the electrons in LiF.

In order to study the influence of the nature of the surfaces on the formation of hollow atoms, we looked, in a second experiment, at the interaction of a same Ar^{17+} ion on metallic and semiconductor targets having the same ionization potential. We have chosen to compare pure polycrystalline gold deposited on a flat silicon wafer and Si(111)-H surfaces (silicon covered with one monolayer of hydrogen) [11], the ionization energies of which are similar (5.5 eV for Au and 5.4 eV for clean or hydrogenated Si surfaces). Instead of studying at grazing incidence the interaction of energetic ions on these surfaces, we fully decelerated down to zero, at roughly normal incidence, the 10 keV/q ions produced by the test Caprice ECR source of the Laboratoire des Ions, des Atomes et des Agrégats (LI2A) in Grenoble. Under such experimental conditions the ion cannot penetrate the solid, and one observes only pure outside or at surface interactions. At such low incident kinetic energies (1 and 2 eV/q), the kinematics of the collision is mainly governed by the image acceleration of these ions and is thus independent of the initial energy. The x-ray spectra emitted in flight by these ions were detected by means of a crystal spectrometer of 6 eV resolution which allowed the separation of all the KL^x satellite lines. The spectra presented in Fig. 3 show dramatic differences in the relative intensity of the KL^1 and KL^2 lines during the interaction of these ions on Si-H and Au targets. The x-ray spectrum observed with the Si-H target displays the very characteristic array of x-ray satellites which is expected and observed [7] for the pure outside decay (KL^x distribution peaked on KL^1). By contrast, the x-ray spectrum obtained with the gold target shows a satellite distribution peaked on the KL^2 line.

More detailed information on the capture processes above surfaces may be obtained by measuring accurately the energy of the KL^x lines. In contrast to what is

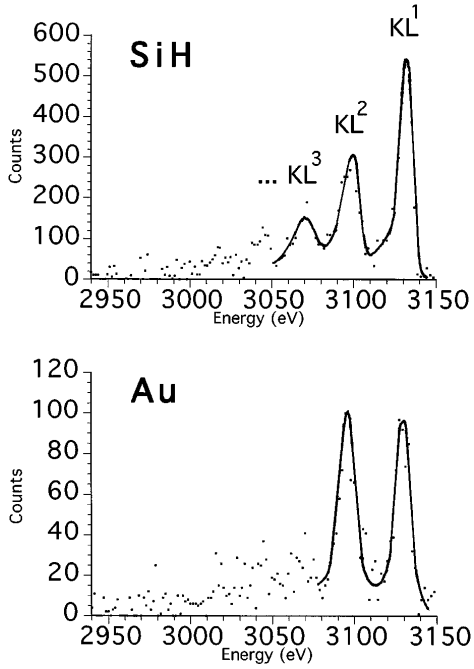

FIG. 3. $K\alpha$ spectra emitted by fully decelerated Ar^{17+} ions (1–2 eV/q) on Au and Si-H targets.

observed below a surface [2], the KL^1 line is narrow and centered at an energy of 3133 eV. Below the surface this line is broad and its energy has been found corresponding to states with a mean value of three M spectator electrons.

In the considered cases, the energy of the KL^1 line corresponds to one (or two) M spectator electron [2] and about two N electrons if only one M electron if present. There may be, in the frame of the "triangular" distribution which is expected outside a surface, few extra electrons in the outermost shells. More detailed spectroscopic information obtained at high resolution when looking at the $K\beta,\gamma$ lines, which will be published in a more extended paper, or have been presented in Ref. [12], also lead to this conclusion that very few $(N, O, \ldots)$ are present at the time of decay. The mean charge of the ion is then quite large during the final approach of the ion above the surface. Moreover, the KL^1 lines observed above metals and insulators show exactly the same energy and width, which means that, in both cases, it corresponds to an outside decay. On the contrary the KL^2 line is broader and its main energy indicates that few more M and/or N electrons are present at the time of the decay.

These findings may be explained with the atomic clock property of the hollow atoms. The relative intensity of the KL^x lines depends only on the rate at which the L shell is filled compared to that for the filling of the K hole. The L filling rate depends, in turn, only on the initial state on which the electrons have been captured during the collision and on the initial number of captured electrons. It decreases slowly with increasing principal quantum numbers n (there are more steps in the Auger cascade for large n) and increases with the number of electrons in the considered shell (the Auger rate scales approximately

with $m^{1.5}$; m being the number of electrons). The binding energy of the target electrons being similar for Au and Si-H surfaces, which implies that according to the over-barrier model capture occurs in approximately the same level of the ion, the increase of the number of L electrons for the metal target could mean that many more electrons have been captured in the same large n states of the ion, increasing then the filling rate of the L shell.

These results may be more likely explained in considering the insulator character of SiH and its effect on the image acceleration first observed by Winter [13]. With an insulator or semiconductor, the removal of valence electrons generates localized positively charged centers, the lifetimes of which are long enough to overcome at normal incidence the image acceleration (the image lies at twice the distance of the ion to the surface). Then the ion may be decelerated and backscattered. One would only observe (Fig. 3) the characteristic pure "outside" decay of the hollow atoms (continuous decrease of the KL^x intensities with increasing values of x). With metals the ions gain some energy (the positive charges are instantaneously screened) and hit the surface. Then they capture more electrons and experience some "at surface" interaction, as described in Ref. [13], leading to direct capture of a few electrons (about three [14]) into the M shell of the ion, like inside the bulk (close collisions). Some of these M shell electrons are very quickly transferred into the L shell through LMM Auger transitions. [The lifetime for such transitions is of the order of $(2–4) \times 10^{-16}$ s [7]; at the considered velocities $\sim 2 \times 10^4$ m s^{-1} the decay then takes place *in situ* along a fraction of angstroms.] The "at surface" interaction leads to an additional and faster filling of the L shell, which increases the intensity of the KL^2 line.

Moreover, at these low velocities, one must point out that the fast Auger transitions decaying the highly excited levels where the electrons are captured ($n > 3$ for outside hollow atoms) and the lifetimes of which are very short (10^{-15} s) reionize *in situ* the ions $[\langle x \rangle = 2 \times 10^4 \times 10^{-15} = 0.2 \times 10^{-10}$ m]. For metals, this reionization can be immediately balanced by a new capture. For insulators the backscattered ions can escape the capture area and be quickly reionized by Auger transitions, without being refed. In such a case, one might observe hollow ions of relatively high charge. Recently, an extreme case of such a process has been observed in the collision of Ar^{17+} on C_{60} [15] where a very large number of electrons is captured mainly without any contact with the target, and all of them (minus one) are ionized by Auger cascades before a K (heliumlike) transition occurs. Hollow atoms are then formed during the collision, but evolve quickly to more ionized states before being observed by looking at the last (inner shells) transition.

In conclusion, we have demonstrated in this Letter that in opposition to the recent claim by Limburg *et al.* we have observed the formation of hollow "atoms" in front of insulator surfaces. As deduced from spectroscopic data, the charge of the projectile is found rather large during the final approach to the surface and the claim must be that hollow *ions* are observed above insulator surfaces. These hollow ions may follow the formation, at ~ 20 Å (z_0) above the surface, of hollow atoms and result from a complex mean equilibrium between ionization through Auger decay and collisional refeeding. We also present the very first spectroscopic signature of a touchdown of an ion on a surface (for metals) and clear indications that above insulators the ion may not touch the surface.

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