Decay time of hollow argon atoms formed below metal and dielectric surfaces

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Slow highly charged ions penetrating surfaces quickly capture many electrons in highly excited states, leaving empty the innermost shells, forming hollow atoms. These hollow atoms then fill their innermost shells in a stepwise manner through a long cascade of Auger and x-ray transitions. We have measured the mean emission depths of the series of x rays emitted during the decay cascade of Ar hollow atoms formed below the surface of metal and dielectric materials. It has been found that the decay times of these hollow atoms are much longer in dielectrics than in metals, and at keV/q kinetic energies, at depths of the order of 10–20 nm, considerably deeper than any expected value. These findings have been tentatively explained by the different responses of metals and dielectrics to the slow penetration of a highly charged ion.

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I. INTRODUCTION

Bare Ar ions penetrating surfaces at low velocities are known [1–3] to capture many electrons in their M and N shells, leaving empty the K and L shells, forming hollow atoms. The spontaneous filling of the L holes of these ions proceeds through the stepwise emission of Auger electrons [4–6] or x rays. We present in this paper measurements of the full decay times of hollow atoms determining the depth of emission of the x rays of Ar ions in metal and dielectric targets, either for the filling of the unique L hole of Ar^{9+} or the stepwise filling of the four or eight holes of Ar^{12+} and Ar^{16+}.

The ions produced by the electron cyclotron resonance (ECR) ion source at the University of Nevada, Reno, were extracted at energies of 5 keV/q and directed at normal incidence to either a gold surface deposited on an atomically flat Si wafer or a germanium single crystal on its 111 crystallographic plane, permanently or sequentially cleaned with an Ar^{1+} ion beam and controlled using the Atomic Clock Property of Hollow Atoms (ACPHA) technique [7]. The x rays emitted by the ions were measured with a SiLi detector in a direction roughly perpendicular to the ion beam (Fig. 1). The mean depth d for the filling of the L shell of the ions was determined measuring the intensity of the x rays transmitted at variable grazing emission angles. The detector was located 13 cm away from the target such that the acceptance angle of detection was of the order of 1.3° and the emission angle θ was defined within ±0.7° in such a way that the projection of the penetration depth would be small enough to be neglected when rotating the targets.

II. THE DECAY DEPTH OF Ar^{9+} IONS

In "neutral" Ar atoms singly ionized in the L shell, the only allowed radiative decay proceeds through the transition of a $3s$ electron into the $2p$ hole. The lifetime of this transition being equal to 3.25 fs [8], the decay length of such atoms traveling at the considered ion velocities would then be equal to 1.5 nm. The electrons captured in the M shell of the ion

own *a priori* any state of angular momentum and one must observe radiative transitions between the $3d$ or $3s$ levels to a $2p$ hole. We present in Fig. 2 the L x-ray spectrum of Ar^{9+} ions emitted in a gold target, at two emission angles, observed with the SiLi detector, i.e., in conditions such that the detailed structure of the complex array of satellite lines corresponding to all substates of population of the M subshells cannot be resolved, and a single line at about 250 eV is observed.

In the case of Ar ions owning eight M electrons the filling of the L hole follows an exponential decay in time $P(t) = \exp(-\lambda t)$ (λ transition probability per unit of time; $\tau = 1/\lambda$: lifetime of the excited level), along a mean emission depth $\langle d \rangle = v\tau$ (v: velocity of the ion), and a transmission at angle θ of the emitted x rays, in a material of linear absorption coefficient μ, given by $\exp(-\mu d/\sin\theta)$. The intensity of the detected x rays decreases with d following $I/I_0 = \exp[-(d/\langle d \rangle + \mu d/\sin\theta)]$. The integration of these probabilities from $d = 0$ up to $d = \infty$ then leads to a total counting rate at a given angle θ and for a mean free path $\langle d \rangle$: $P(\theta,\langle d \rangle) = 1/[1/\langle d \rangle + \mu/\sin\theta]$.

The filling of the L hole of Ar^{9+} ions may hold at any time of the filling of the M shell. Let T_m be the time needed for an ion already owning m M electrons to capture one more electron, and τ_m the decay time for an ion owning m M electrons to fill its L hole. While the filling of the L shell from M^8 states may freely last all during its exponential decay, the L shell filling at the previous steps ($M^{7,6L}$) is always interrupted by further electron captures, and must not last more than the time T_m before the ion captures one more electron (Fig. 3), substantially lengthening the emission depths.

The filling rate of the M shell through Auger neutralization [3] is, in first approximation, proportional to the number of M holes [1]; the M shell filling times T_m then roughly linearly lengthen with the number m of M electrons present in the ion. The lifetimes τ_m of the L shell filling, at each state of the stepwise filling of the M shell, decrease (shorten) when processing through spontaneous Auger transitions, as the inverse of the square of the number m of M electrons [9]. The filling of the L hole then holds along a more or less extended range below the surface, depending on the filling
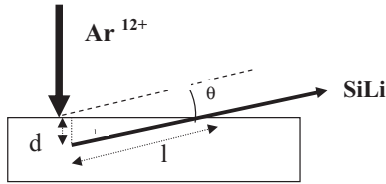
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FIG. 1. Schematic of the tuning of the photon absorption length by rotating the target at an angle θ with respect to the surface of the solid target.

rate of the M shell, displaying a broad maximum versus depth (Fig. 3).

On gold targets ($\mu = 0.027$ nm^{-1}) we measured a ratio of the number of detected x rays of 0.6 ± 0.03, between angles $4.3°$ and $22.3°$ (Fig. 2), while the calculated value according to the hypothesis of an instantaneous neutralization of the M shell, i.e., mean decay $\langle d \rangle = 1.5$ nm, is equal to 0.71. The x rays are then experimentally only slightly more absorbed, which means that the ion mean decay depth is only slightly longer, of the order of 2.1 ± 0.3 nm.

Highly charged ions entering a metal are actually very quickly surrounded by a cloud of free electrons to be quasineutralized in the volume of a Debye sphere, an effect already experimentally demonstrated [10]. It is not then surprising to observe that the M shell of the Ar^{9+} ions entering a metal is very quickly closed through Auger neutralization processes with electrons of the *conduction* band of the solid.

We measured in Ge targets ($\mu = 0.018$ nm^{-1}) a ratio of the detected intensities of x rays emitted at $3°$ and $30°$ of 0.25 ± 0.04 (instead of a calculated value of absorption of 0.59 assuming an instantaneous closing of the M shell followed by the decay of a neutral atom ionized in its L shell), which means that the emission holds much more deeply in Ge than in Au. The mean emission depth of this much slower series of events which shows a broad maximum (Fig. 3) has been found, using the same mean depth definition as that for metals, to be of the order of 9 nm.

This unexpected huge emission depth clearly shows that the M shell is very slowly filled inside the Ge target compared to the gold target. The Auger Neutralization (AN) process is a collective interaction at low velocity of an ion with a solid (the ion becomes part of the solid), in which an electron of the
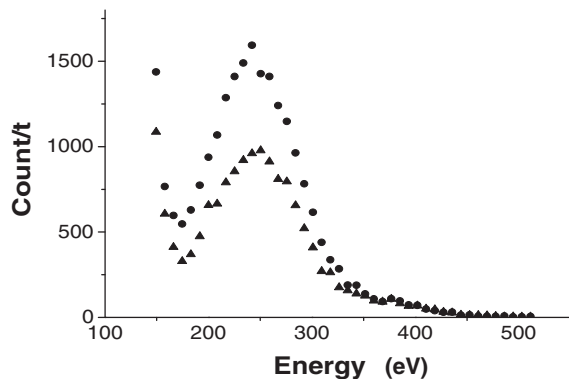

FIG. 2. L x-ray spectrum of Ar^{9+} ions inside a gold target: circles at an emission angle of $22.3°$ and triangles at $4.3°$.
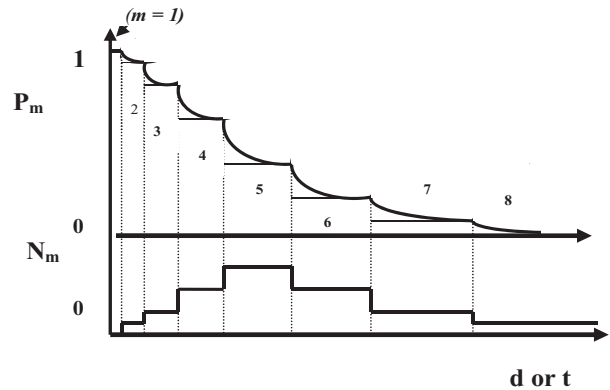

FIG. 3. P_m (top): probability of finding the ion in a state with m M electrons versus depth d or time t. N_m (bottom): mean decay rate in state m.

valence or conduction band of the target is transferred into an empty level of the ion [3]. The transition rate of this "Auger-type" decay obviously increases with the density of states of the initial state (much higher in a metal than in dielectrics) and may then explain why fewer electrons are present at the time of the filling of the L hole in Ge than in gold ($\langle m \rangle = 4$).

III. THE DECAY DEPTH OF Ar^{12+} IONS

The same experiments have been carried out with Ar ions owning four and eight holes in the L shell (Ar^{12+} and Ar^{16+}). In that case the intrinsic lifetimes τ, or the mean decay depths d, for the filling of the *first L* hole, linearly decrease [1], when the number of L vacancies increases, the full filling of the L shell proceeding then through a series of steps of increasing lifetimes.

In Au targets, the mean depth for the filling of the "first" L hole of Ar^{12+} would then be of the order of that for Ar^{9+} divided by 4: 1.5 nm/4 = 0.4 nm (for ions with a closed M shell), i.e., very small. The filling of the M shell is not, however, completed at these very first moments of the interaction, even inside metals. In metals the M shell has been found to be quasiclosed for Ar^{9+} ions along a depth of 0.6 nm, and one can safely expect that the mean decay depth for the filling of the *first L* hole of Ar^{12+} in gold would be of the order of 0.8 ± 0.3 nm.

In Ge targets one can expect the same shortening of the decay depths due to the increasing number of L holes, associated with a slower M shell filling. As the filling rate of a L hole increases with the number of M electrons, the largest expected decay depth corresponds to the smallest number of M electrons. The minimum number of M electrons allowing a *LMM* Auger transition (99.9% of the decays), $m = 2$, corresponds according to the scaling laws [1], to the largest *possible* expected decay depth: 6.5 nm for the filling of the first L hole of Ar^{12+}. The mean decay depth for Ar^{9+} in Ge being 9 nm as quoted above, corresponding to a mean occupation of the M shell of $\langle m \rangle = 4$, one can expect for Ar^{12+} (the AN rate for the filling of the M shell only depending on the number of M electrons present in this shell, and the density of states of the conduction or valence band of the target) a mean decay depth of approximately 9nm/4 = 2.25 nm. Taking account
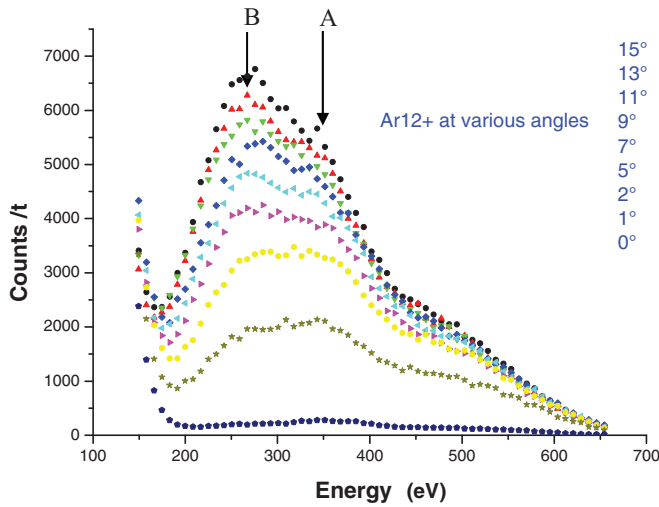
FIG. 4. (Color online) X-ray spectra emitted by Ar^{12+} ions impinging on a gold surface at various incidence angles (top to bottom: 15°–0°) showing the splitting of the spectrum into two separate peaks, A and B.

FIG. 5. (Color online) Typical decay curves versus time of the four L^n transitions (n number of L electrons) stepwise filling the four L holes of an Ar^{12+} ion whose lifetimes increase according to scaling laws [1] (arbitrary units).

of the known small differences between the calculated values deduced from the most elaborate programs, and the predictions of the scaling laws for Ar ions [1] the uncertainty on the mean number of M electrons may be estimated to be of the order of $\Delta \langle m \rangle = 1$, i.e., a maximum value of 4 nm.

The L x-ray spectrum of hollow atoms formed with Ar^{12+} ions is made of four L^x satellite lines (x number of L electrons) corresponding to each of the stepwise transitions filling the four L holes. Below the surface the ion ends its decay as a quasineutral atom and all L^x lines are present in the spectrum. The L^x lines are separated in energy by about 35 eV and extend between 220 and 350 eV and cannot be resolved with a SiLi detector.

The transmission of the window of the detector actually drops at the carbon K threshold at 285 eV, transforming a uniform unresolved spectrum into two main peaks on both sides of this threshold (Fig. 4). The low-energy peak, hereafter designated as B, comprises the lines of the two satellites L^7 and L^6 (signing the last two steps of the L shell filling), and the higher-energy peak, designated as A, the two L^5 and L^4 satellites (first two steps of the L shell filling). The absorption of x rays by this window helps then to separate the two extreme L components of the spectrum (only relative values of the counting rates on each side of the C K threshold have been used in the data analysis).

The timing of the filling of the last two holes (B line) does not follow an exponential decay law as the very first one because ions in these states have first to accumulate in time before decaying (Fig. 5), following a time evolution given by the Bateman equations [11]. The much more extended decay depths of these last steps then hold much deeper.

In gold (Fig. 4) one finds from the variation of the counting rates versus the emission angle that the mean decay depth of the A line is of the order of $\langle d_A \rangle = 1.7 \pm 0.6$ nm, and that the B line is more absorbed than the first one (A) and then decays deeper, illustrating the validity of the technique. As quoted above the expected mean decay depth of the *first*
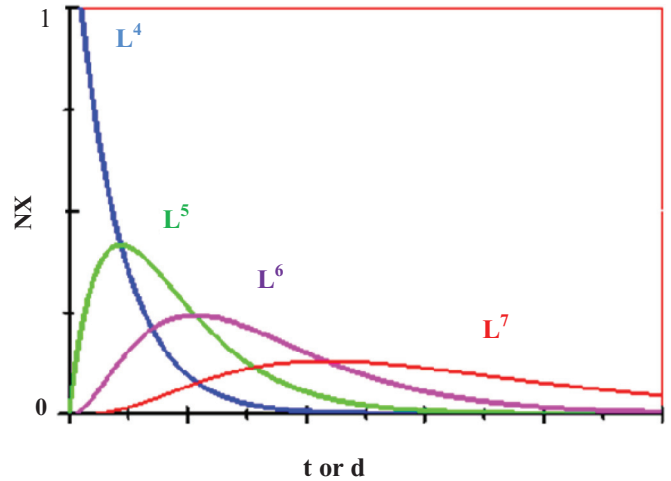
(L^4) transition would be, according to the scaling laws, of the order of 0.8 ± 0.3 nm, but the second transition (L^5) must experimentally slightly lengthen the measured mean decay depth of the whole A line according to its nonexponential decay. The addition of the L^4 and L^5 lines of Fig. 5 leads to a nonmonotonic decay curve close to that of an exponential fitting with a mean depth 50% larger. The experimental mean decay depth is then slightly longer than expected: 1.2 nm. The same general trend has also been observed for Ar^{16+}: $\langle d_A \rangle = 6$ nm.

In dielectrics we found a mean decay depth for the whole A line ($L^4 + L^5$ satellites), $\langle d_A \rangle = 17$ nm, and a much deeper value for the B line ($L^6 + L^7$) whose exact value cannot be significantly given. The mean decay depth for the A line $\langle d_A \rangle$ has to be compared to an expected decay depth for the L^4 line of 2.25 nm, which would, as explained above, lead to an approximate decay depth for the whole A line of 3.4 nm, i.e., five times deeper than expected.

The filling of the L holes mainly proceeds through (LMM) Auger transitions. Each LMM Auger transition filling a L hole re-ionizes twice the M shell of the ion leading, before any refilling of the M shell, to a large lengthening of the lifetime of the next transition (the Auger transitions scale as m^2 [9], the lifetime for the filling of, e.g., a second hole in the L shell would then be strongly lengthened.

In gold targets, where the measured decay depth is only about two times longer than expected, the filling of the M shell is so fast that this effect may not dramatically change the decay depth, by contrast to what happens in dielectrics (Ge) where the filling of the M shell has been found to be much slower, strongly lengthening the decay depth.

The huge increase of the mean emission depth in dielectrics, explained as discussed above for Ar^{9+} by a slower filling of the M shell, may then be at least partly dramatically enhanced for ions owning a certain number of L vacancies by this re-ionization of the M shell at each step of the filling of the L shell.

Pesic *et al.* [12] recently measured, using a technique similar to ours, the relaxation time of Pb^{53+} ions in *metal* (Ta) foils, which they found much longer than expected, an effect they explained by the formation of molecular orbitals in these *symmetric Pb/Ta* couples. Such processes cannot, however, be considered in the very *asymmetric* ions–solid-atom couple of the present experiment, in a *dielectric* target.

IV. CONCLUSIONS

We present in this paper experiments in which we measured the approximate absolute mean depth at which the filling of the single L hole of Ar^{9+} entering a solid takes place, 2.1 nm in Au, showing a quick filling of the M shell, and 9 nm in Ge, very far away from any expected values to date, explained by a much slower filling of the M shell by electrons of the *valence* band of the solid. These experiments have also been carried out with Ar ions owning four and eight L holes, measuring the mean decay depths of the cascade of transitions filling the L shell and found to be much deeper than expected in dielectrics, such enhanced effect being at least partly explained by the re-ionization of the M shell after each LMM Auger transition filling a L hole. These findings may then lead to the reconsideration of some of the conclusions drawn from previous experiments in Auger spectroscopy on slow, highly charged ion interaction with surfaces (as already pointed out in Ref. [13]), or even the modeling of the charge state evolution or equilibrium of ions passing through thin foils.

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