

Al atomic Auger electron emission from low-keV-ion-bombarded Al surfaces

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Al atomic *LMM* Auger electron emission from clean and oxygen- or argon-covered Al surfaces has been studied for low-keV Ar^+ -ion bombardment along normal and off-normal incidence directions. We show that, for a clean Al surface, many transitions are suppressed by the surface-neutralization process and that the quenching of such a neutralization mechanism and the activation of a surface-ionization mechanism by oxygen chemisorption or argon physisorption can unveil these hidden peaks. Our results provide some insights into the peculiarities of ion-solid interactions and offer an interesting explanation to the observed large difference in the relative transition ratios in experiments with solid and gas targets.

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I. INTRODUCTION

During collisions between two atomic particles, core electrons of one or both colliding partners can be ionized or excited into high-lying empty levels if the closest approach distance is smaller than a critical value, as suggested by the molecular-orbital-crossing model of Fano and Lichten [1] and of Barat and Lichten [2]. The subsequent Auger decay can give rise to a large number of transition lines in the detected electron spectra. The identification and investigation of the relative intensities of these atomic peaks have been the subject of intense studies in the last 20 years [3–5].

On the other side, the incomparably high atomic densities of solid surfaces relative to gas targets has resulted in an increasing interest of the scientific community in studies of Auger electron emission by ion impact on solid surfaces [6–9]. By correlating the variation of the measured kinetic energies to that of the surface work function, Zampieri and Baragiola demonstrated that all narrow transition lines are due to decays in the sputtered target or scattered projectile particles taking place in the vacuum [10]. However, the interactions between excited leaving particles and the solid surface can render the deexcitation process much more complicated. Indeed, the relative intensity ratios between various atomic features in the detected Auger electron spectra differ substantially from those obtained for gas targets and many transition lines have not been observed at all for solid targets [11]. Zampieri and Baragiola detected only two Ne Auger lines by bombarding an Al surface with Ne^+ ions and attributed the absence of other peaks to surface resonant charge-transfer effects [12].

In this paper we report an investigation on Al atomic Auger electron emission for Ar^+ -ion impact on a clean Al surface and oxygen- or argon-covered Al surfaces. The choice of Al was based on the consideration that there exist extensive studies in the literature and its major spectroscopic structures have all been identified previously and that gas-phase Auger spectra are also available [11,13]. Our results show that the relative transition ratio is a strong function of the surface condition of the

sample and many peaks absent in the case of clean Al are clearly present if the electronic and chemical properties of the surface are appropriately altered. We provide conclusive evidence that the solid-particle charge-transfer mechanism is an important cause for the observed large difference in the relative transition ratios for solid and gas targets and offer an interesting insight into the peculiarities of solid-particle interactions.

II. EXPERIMENT

The experiments were performed in an UHV chamber with a base pressure in the 10^{-10} -Torr range. A mechanically polished pure polycrystalline Al sample was mounted on a dedicated manipulator which could be rotated to change the ion-incidence angle. Sample cleaning was accomplished by *in situ* ion bombardment. Projectile Ar^+ ions with energies of 2–15 keV were produced by a differentially pumped ion gun and the beam current density ranged from 10 to 80 $\mu\text{A}/\text{cm}^2$ as measured by a Faraday cup. An Al disk was attached to a cold finger with He cycling to serve as the substrate for Ar condensation.

Argon gas, introduced into the chamber through a gas line, could be sprayed directly onto the cold target at a distance of about 8 mm while oxygen gas was admitted through a different gas line and allowed to fill the whole chamber uniformly. Since ion bombardment by itself is an erosive process, all measurements were conducted in dynamic equilibrium situations with beam and vacuum pumps on and the gas line open. The actual coverage depends on the local partial pressure, on the beam current density, and on the sputtering yield which is related to the primary energy. For the results presented in this paper only qualitative meanings are assumed for the coverages.

Emitted Auger electrons were collected by a hemispherical energy analyzer working in a constant-pass-energy mode (20 eV) and situated at 70° relative to the ion beam direction. Spectra were collected in the pulse-counting mode with a computer-aided measurement and

control data-acquisition system. Details of our experimental setup have been given elsewhere [14,15].

III. RESULTS AND DISCUSSIONS

In Fig. 1 we present some Al spectra for 15-keV Ar^+ -ion bombardment on clean and oxygen- or argon-covered Al surfaces for both normal and off-normal incidence directions. All these spectra have been corrected for spectrometer-transmission factor, background subtracted with a third-degree polynomial matching a large number of data points on both ends, and normalized to the same height. These results clearly show the dependence of the relative transition ratios on the surface conditions.

Let us first note that for the spectra obtained from the clean Al sample, the intensity ratios between different atomic peaks show a slight change for $E_p \leq 3$ keV and remain constant thereafter up to 15 keV. Whaley and Thomas assigned the most intense peak at 62.6 eV (labeled *G* in Fig. 1) to $2p^5 3s^2 3p^2 \rightarrow 2p^6 (3s 3p^3 P)$ autoionization in a neutral Al^* atom and the other two structures at 55.5 (peak *D*) and 48.8 eV (peak *B*) to Auger transitions from the initial $2p^5 3s^2 3p$ state to final $2p^6 3s$ and $2p^6 3p$ configurations in an inner-shell-excited Al^+ ion, re-

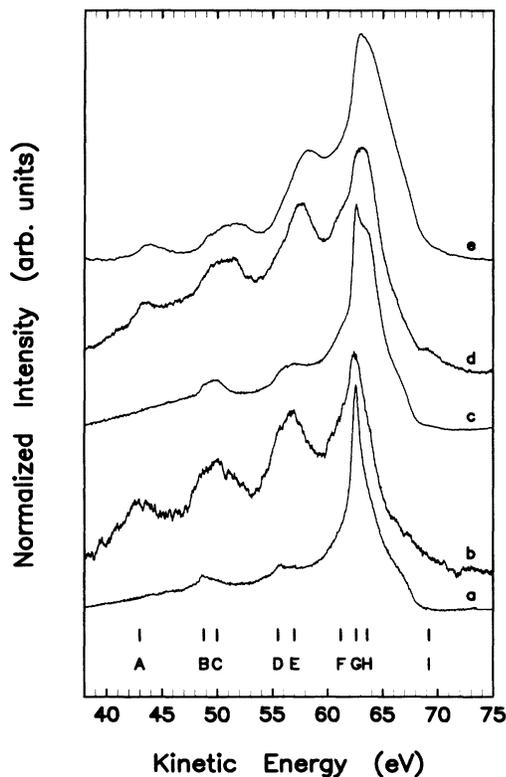


FIG. 1. Background-subtracted, spectrometer-transmission-factor corrected, and normalized Al Auger spectra taken by 15-keV Ar^+ -ion impact on clean Al surface at $\theta_i = 0^\circ$ (curve *a*); oxygen-covered Al at $\theta_i = 0^\circ$ (curve *b*); clean Al at $\theta_i = 45^\circ$ (curve *c*); oxygen-covered Al at $\theta_i = 45^\circ$ (curve *d*); and argon-covered Al at $\theta_i = 45^\circ$ (curve *e*). The tick marks indicate the energy positions of the atomic peaks.

spectively [11]. They suggested that the feature *D* probably also contains contribution from the $2p^5 3s^2 3p^3 \rightarrow 2p^6 3p^2 ({}^3P)$ transition.

A careful analysis of our Al spectra recorded in the pulse-counting mode with an improved energy resolution (~ 0.2 eV) and magnified for each individual spectral region (see the bottom two curves in the four panels of Fig. 2) reveals that all these features undergo a considerable asymmetric broadening toward high energies as the primary ion energy E_p is raised from 2 to 3 keV. Detailed line-shape curve fittings following the procedure proposed by Whaley and Thomas [11] further indicate the presence of a shoulder at 61.3 eV even at the lowest primary energy studied ($E_p = 2$ keV). These components may be attributed either to the Doppler shifts due to a possible increase in the average velocity of the ejected excited Al particles in this range of E_p or to the appearance of other transition lines whose intensities for some reason are greatly reduced at 2 keV.

The presence of only three clearly resolved atomiclike Auger features for Ar^+ -ion impact on a solid Al target in comparison to at least ten well-resolved lines in the spectra obtained by Dahl *et al.* in a gas-phase 50-keV Al^+ -Ar experiment [13] has been a puzzle for a long time. Though observation of many doubly-core-excited-Al L^2 -LMM Auger transitions has been recently reported by us for off-normal Ar^+ -ion incidence on a clean Al sample [14,16], several other predicted transitions, especially those from the initial core-excited Al^{2+} states, are not detected yet. Since core-electron excitation in ion-solid collisions is governed by the same mechanism for binary

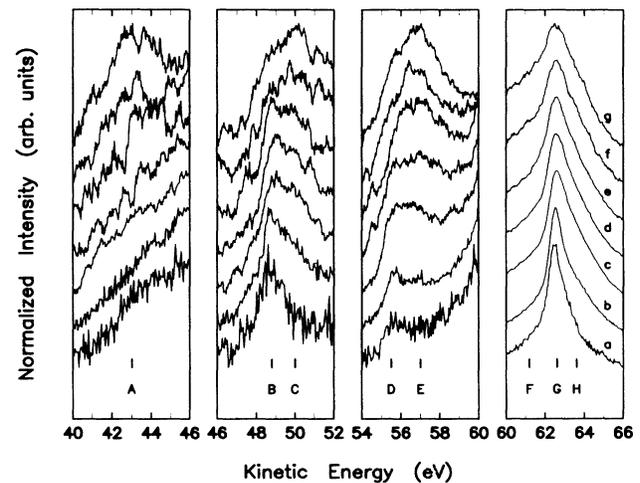


FIG. 2. Al Auger spectra taken from Ar^+ bombardment along the surface normal on Al surfaces with $E_p = 2$ keV (curve *a*) and $E_p = 15$ keV (curves *b*–*g*) at oxygen pressure of $P_{\text{O}_2} = 0$ (curve *a*); $P_{\text{O}_2} = 0$ (curve *b*); $P_{\text{O}_2} = 3 \times 10^{-7}$ Torr (curve *c*); $P_{\text{O}_2} = 6 \times 10^{-7}$ Torr (curve *d*); $P_{\text{O}_2} = 1 \times 10^{-6}$ Torr (curve *e*); $P_{\text{O}_2} = 2 \times 10^{-6}$ Torr (curve *f*); $P_{\text{O}_2} = 3 \times 10^{-6}$ Torr (curve *g*). All the spectra with oxygen exposure have been corrected for shifts due to changes in the surface work function (~ 0.1 eV) and normalized for each individual spectral region.

ion-atom encounters (promotion of molecular orbitals), the absence of the others should be related to the difference in the deexcitation mechanisms, more specifically, to the interactions between the core-excited Al particles and the metal surface.

Some 30 years ago, Hagstrum suggested that an ion in the vicinity of a metal surface can be neutralized by capturing a valence electron from a solid via a resonant tunneling or an Auger process if the atomic binding energy is larger than the surface work function and that a neutral atom can be ionized through a reverse charge-transfer mechanism if the energy relationship is reversed [17,18]. Because the binding energy of 16.34 eV for a 3p electron in an inner-shell-excited Al⁺ ion ($2p^5 3s^2 3p$), estimated to be equal to the second ionization energy of Si (Refs. [13,19,20]), is much larger than the surface work function of the clean Al (4.28 eV, Ref. [21]), virtually all the escaping Al²⁺ ions with an electronic configuration of $2p^5 3s^2$ will capture a valence electron into their empty 3p levels before they decay in the vacuum. Similarly, Al²⁺ ions in the $2p^5 3s 3p$ and in the $2p^5 3p^2$ configurations will also alter their initial states on their way out of the sample, thus no Al²⁺ Auger transitions can be observed for a solid Al target. On the other side, the ionization energy of an inner-shell-excited Al neutral atom ($2p^5 3s^2 3p^2$), estimated as equal to that for a ground-state Si (8.18 eV, Refs. [13,19,20]), is still large enough in comparison to the Al work function so that an inner-shell-excited Al⁺ ion moving in the vicinity of an Al surface can be neutralized via a resonant tunneling or an Auger process and its subsequent decay will contribute to the Al* autoionization lines.

In order to reveal these hidden peaks it is necessary to minimize the neutralization processes and maximize the ionization ones. For this purpose, we exposed the clean Al surface to an increasing amount of oxygen at room temperature while keeping the primary ion energy and the beam current constant. A set of spectra taken for 15-keV Ar⁺ impact along the surface normal are shown in Fig. 2 for four spectral regions.

The spectra in Fig. 2 show the clear appearance and

the gradual growth of three new Auger lines A, C, and E as the effective O₂ coverage increases. These peaks, observed only by modifying the surface electronic and chemical properties, should be attributed to transitions from initial Al⁺ or Al²⁺ ions. Using the binding energies of Shirley *et al.* [20] and of Moore [19], we calculated the predicted Auger electron kinetic energies for transitions occurring in an inner-shell-excited Al⁺ ion. For energies of autoionization in Al* neutral atoms and in inner-shell-excited Al²⁺ ions we followed the Z+1 rule prescribed by Dahl *et al.* [13] and by Whaley and Thomas [11] (the errors in these cases can be around 1 eV). A comparison with the predicted kinetic energies leads us to attribute the peaks A, C, and E to Auger transitions $2p^5 3s^2 \rightarrow 2p^6$, $2p^5(3s 3p^3 P) \rightarrow 2p^6$, and $2p^5(3p^2^1 D) \rightarrow 2p^6$ in Al²⁺ ions, respectively. For a better identification of the atomic lines, the kinetic energies of all observed peaks are listed in Table I in which energy differences relative to the main autoionization peak are also included since the absolute energy positions may be influenced by the spectrometer work function. We point out that the nonuniformity of the effective oxygen coverage over the sample surface caused by the nonuniformity of the ion beam current density (which has a Gaussian profile) can result in a broadening of all the atomic lines as indeed is observed. This broadening may smear out many otherwise probably resolvable atomic transition lines.

Early photoemission studies on oxygen chemisorption on clean Al showed a gradual increase of the density of the O 2p-derived valence-band states in the energy range of 8–16 eV below the vacuum level and a simultaneous decrease of the electron density near the Fermi level as oxygen coverage increases [22,23]. Upon heavy oxidation (> 50 L, 1L=10⁻⁶ Torr sec) there is clear evidence of Al₂O₃ oxide formation [24,25]. In the vicinity of a solid surface, the binding energy of an ion can be reduced by up to 1–2 eV because of the image potential created in the surface [26]. It is clear that the effect of oxygen is then to dramatically reduce the probability of charge transfer from the solid to the excited Al⁺ particles, thus to reduce the autoionization signal of Al⁰. On the other

TABLE I. Atomiclike Auger transitions in Al (all energies are in eV).

Peak label	Initial charge state	Transition	Predicted E_k^a	Observed E_k	Observed Relative E_k
A	Al ²⁺	$2p^5 3s^2 \rightarrow 2p^6$	43.8	43.0	-19.6
B	Al ⁺	$2p^5 3s^2 3p \rightarrow 2p^6 3p$	48.83	48.8	-13.8
C	Al ²⁺	$2p^5(3s 3p^3 P) \rightarrow 2p^6$	50.0	50.0	-12.6
D	Al ⁺	$2p^5 3s^2 3p \rightarrow 2p^6 3s$	55.5	55.5	-7.1
E	Al ²⁺	$2p^5(3p^2^1 D) \rightarrow 2p^6$	58.5	57.0	-5.6
F	Al ⁺	$2p^5(3s 3p^2^4 P) \rightarrow 2p^6 3s$	61.4	61.2	-1.4
G	Al ⁰	$2p^5 3s^2(3p^2^3 P) \rightarrow 2p^6(3s 3p^3 P)$	61.5	62.6	0.0
H	Al ⁰	$2p^5 3s^2(3p^2^1 D) \rightarrow 2p^6(3s 3p^3 P)$	62.3	63.6	1.0
I	Al ²⁺	$2p^4(1 D) 3s^2 3p \rightarrow 2p^5 3s$	66.8 ^b	69.2	6.6

^aThe predicted kinetic energies are all calculated for the initial 2p state with $j = \frac{3}{2}$. The spin-orbit splitting for Al 2p is 0.4 eV and in the present study these two components are not resolved. For Al⁺ states, binding energies of Shirley *et al.* [20] and Moore [19] are used and for those of Al⁰ and Al²⁺ states, the Z+1 rule is applied [11,13].

^bValue taken from Ref. [13].

side, ion bombardment creates a great number of defects in the oxide causing the presence of a large number of empty states either in the oxide gap [27] or in the O $2p$ -derived valence band with binding energies nearly resonant with or larger than that of the $Al^+ 3p$ level. The presence of these empty states, whose number is proportional to the oxygen coverage, greatly favors the further ionization of the inner-shell-excited Al^+ ions into Al^{2+} . Of course, the outgoing Al^{2+} ions with a core hole ($3p$ binding energy is 16.34 eV) will most probably be neutralized by valence electrons. However, for E_p as low as 15 keV, the number of leaving Al^+ ions is much larger than that of Al^{2+} , so the net effect is an ionization of Al^+ ions into Al^{2+} giving rise to the appearance of the hidden Al^{2+} -related Auger peaks.

It should be mentioned that, as suggested by Zampieri and Baragiola [10], the kinetic energy of the Auger electrons emitted in the vicinity of a solid surface should be rigidly shifted according to the variation in the surface work function. Our spectra show that the most intense Al autoionization feature undergoes a downward shift of no more than 0.15 eV upon oxygen chemisorption, in agreement with the previous studies which established that chemisorbed oxygen is incorporated in the Al matrix and has little influence on the surface work function ($\Delta\Phi \leq 0.2$ eV [28]). To better emphasize the changes in the line shape, all spectra with O_2 deposition in Fig. 2 have been corrected for this shift.

The evolution of these spectroscopic features also clarifies the ambiguity in the identification of peak D and provides interesting information on the nature of the line-shape broadening observed already for clean Al. Indeed, the behavior of the intensity ratio between peaks D and G as a function of oxygen exposure excludes any possibility of assignment of D to an autoionization. Transitions C , E , and F can be really present in the spectrum obtained by 15-keV Ar^+ and their absence in that for $E_p = 2$ keV may again be attributed to the surface neutralization since the lowering of the average velocity of the ejected Al^+ (Al^{2+}) ions will increase the probability of the charge-transfer process. As far as the feature H is concerned, a possible $2p^5 3s^2(3p^2 1D) \rightarrow 2p^2(3s 3p^3 P)$ autoionization may be assigned. Its relative intensity with respect to the main peak G does not have any detectable variation as a function of oxygen partial pressure given that their initial states differ only for spin-orbit-interaction configurations. Nevertheless, this argument does not exclude at all the Doppler effects as a possible source for the broadening of all peaks seen at $E_p = 15$ keV relative to $E_p = 2$ keV.

For off-normal ion incidence on oxygen-covered Al (see

curve d of Fig. 1), a fourth peak (labeled I) at 69.2 eV can be clearly resolved. Considering that this feature is observed only for $\theta_i \neq 0^\circ$, we tentatively assign it to a $2p^4(1D)3s^2 3p \rightarrow 2p^5 3s$ transition since for low E_p , double core excitation in Al can be produced only in primary asymmetric collisions with incoming Ar particles [14].

To further investigate the importance of the solid-particle interactions on the alternation of the initial excited configurations of the atomic lines, we condensed inert argon gas on a clean Al substrate at 20 K. The line-shape variation of the so-obtained Al spectra is quite similar to that for oxygen chemisorption. In this case, the frozen noble-gas layer does not alter the electronic structure of the underlying Al substrate but serves as a buffer medium in such a way that the ion-metal charge-transfer effects are largely reduced. In fact, in ion-atom interactions, electron resonant transfer is very unlikely unless the two levels are perfectly resonant because of the high localization of these atomic orbitals (the Auger neutralization of the $Al^{2+} 3s$ is energetically forbidden and the radiation decay has negligible probabilities). We mention that, however, to obtain a large variation in the relative intensity ratios as the curve e of Fig. 1, virtually the whole Al surface should be covered by argon so that the incoming Ar^+ projectile particles can no longer directly hit the substrate Al atoms. The decrease in Ar-Al collision energies also causes a great reduction in the probability of Al double core excitation with respect to that of single core excitation causing the absence of peak I in our spectra.

IV. CONCLUSIONS

In summary, we have reported a study on the Al atomic Auger and autoionization peaks by bombarding clean and oxygen- or argon-covered Al surfaces. We have shown that many transition lines originating from the initial Al^+ and Al^{2+} ions cannot be detected for clean Al surfaces because of the strong surface-neutralization effects and the quenching of such a neutralization mechanism and the activation of a surface-ionization mechanism can restore these decay channels. Our results offer an interesting explanation for the very different relative transition ratios in ion-solid and ion-atom collision experiments.

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[1] U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965).
 [2] M. Barat and W. Lichten, Phys. Rev. A **6**, 211 (1972).
 [3] N. Stolterfoht, Phys. Rep. **146**, 315 (1987).
 [4] L. O. Werme, T. Bergmark, and K. Siegbahn, Phys. Scr. **8**, 149 (1973).
 [5] E. T. McGuire, Phys. Rev. A **11**, 1880 (1975).

[6] E. W. Thomas, Vacuum **34**, 1031 (1984).
 [7] J. A. D. Matthew, Phys. Scr. T **6**, 79 (1983).
 [8] N. Benazeth, Nucl. Instrum. Methods **194**, 405 (1982).
 [9] A. Bonanno, F. Xu, M. Camarca, R. Siciliano, and A. Oliva, Phys. Rev. B **41**, 12 590 (1990).
 [10] G. E. Zampieri and R. A. Baragiola, Phys. Rev. B **29**,

- 1480 (1984).
- [11] R. Whaley and E. W. Thomas, *J. Appl. Phys.* **56**, 1505 (1984).
- [12] G. E. Zampieri and R. A. Baragiola, *Surf. Sci.* **114**, L15 (1982).
- [13] P. Dahl, M. Rodbro, G. Hermann, B. Fastrup, and M. E. Rudd, *J. Phys.* **B 9**, 1581 (1976).
- [14] F. Xu, M. Camarca, A. Oliva, N. Mandarino, P. Zoccali, and A. Bonanno, *Surf. Sci.* **247**, 13 (1991).
- [15] F. Xu and A. Bonanno (unpublished).
- [16] F. Xu, F. Ascione, and A. Bonanno (unpublished).
- [17] H. D. Hagstrum, *Phys. Rev.* **96**, 336 (1954).
- [18] H. D. Hagstrum, in *Inelastic Ion-Surface Collisions*, edited by N. H. Tolk, J. C. Tully, W. Heiland, and C. W. White (Academic, New York, 1977).
- [19] C. E. Moore, *Natl. Bur. Stand. (U.S.) Circ. No. 467* (U.S. GPO, Washington, DC, 1949).
- [20] D. A. Shirley, R. L. Martin, S. P. Kowalczyk, F. R. McFeely, and L. Ley, *Phys. Rev. B* **15**, 544 (1977).
- [21] *CRC Handbook of Physics and Chemistry*, edited by R. C. Weast, 65th ed. (CRC, Boca Raton, 1985).
- [22] K. Y. Yu, J. N. Miller, P. Chye, W. E. Spicer, N. D. Lang, and A. R. Williams, *Phys. Rev. B* **14**, 1446 (1976).
- [23] W. Eberhardt and C. Kunz, *Surf. Sci.* **75**, 709 (1978).
- [24] J. E. Crowell, L. J. Chen, and J. T. Yates, Jr., *Surf. Sci.* **165**, 37 (1986).
- [25] C. F. McConville, D. L. Seymour, D. P. Woodruff, and S. Bao, *Surf. Sci.* **188**, 1 (1987).
- [26] *The Oxide Handbook*, edited by G. V. Samsonov (IFI/Plenum, New York, 1973).
- [27] R. Kumar, M. H. Mintz, and J. W. Rabalais, *Surf. Sci.* **147**, 15 (1984).
- [28] A. M. Bradshaw, P. Hofmann, and W. Wyrobisch, *Surf. Sci.* **68**, 269 (1977).