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Interaction of molecular oxygen ions with copper surface: features of the energy spectra of sputtered and backscattered ions

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An experimental study on the energy spectra of ions emitted from the surface of a polycrystalline Cu target under the bombardment by 2 keV O_2^+ molecular ions was carried out. Sputtered atomic ions Cu^+ and O^+ were prevailed among the positively charged secondary ions, and among the negative ions, in addition to sputtered ions Cu^-, CuO_2^-, O^-, and O_2^-, intense elastically and inelastically backscattered O^-, and O_2^+ ions were revealed.

Keywords: energy spectra, ion sputtering, backscattered ions, charge exchange.

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The interaction of low-energy oxygen ions and atoms with the surface of solids is accompanied by a number of processes, including sputtering (etching) of the bombarded target and scattering of oxygen ions. Sputtering by O_2^+ ions is used efficiently in secondary ion mass spectrometry (SIMS) [1] to enhance the sensitivity of this method by increasing the ion yield of electropositive impurities. In the case of low-energy ion scattering (LEIS) [2,3], ions of inert gases (He^+, Ne^+), which provide a unique sensitivity to the composition and structure of the uppermost layer, and ions of alkali metals (Na^+, Cs^+), which allow one to perform quantitative elemental surface analysis, are preferred. The scattering of beams of oxygen atoms and ions off the surface of metals (Mg, Al, and Ag) [4], semiconductor Si crystals [5], and ionic LiF crystals [6] has been studied extensively in the late 1990s. These studies were mostly theoretical and directed at identifying the mechanisms of production of negative oxygen ions (charge exchange), while experiments were performed at grazing incidence angles and small scattering angles (no higher than 40°). This extended the time of interaction between bombarding particles and the surface atoms. The theoretical and applied interest in the processes of production of negative oxygen ions was stimulated by the prospects of development of efficient sources of negative ions and still remains strong (see, e.g., [7] and references therein).

The aim of the present study is to examine experimentally the specific features of energy spectra of sputtered and scattered ions produced under bombardment of the surface of a polycrystalline copper target by molecular $^{16}O_2^+$ ions with an energy of 2 keV (1 keV/atom). The spectra of both positive and negative sputtered and backscattered ions were measured almost simultaneously in the direction perpendicular to the target surface.

Polished samples of high-purity polycrystalline copper were used as targets; experiments were performed at Istituto per l'Energetica e le Interfasi (CNR-IENI, Padua, Italy) in a high-vacuum multifunctional setup equipped with a Hiden EQS 1000 quadrupole mass–energy analyzer and a DP50B (VG Fison) duoplasmatron ion source. This setup was described in detail in [8]. The schematic diagram of the experiment geometry is presented in Fig. 1. The key feature of the setup is its capacity to measure mass spectra (in terms of ratio M/q of the ion mass to its charge at a fixed energy) and energy spectra (at a fixed M/q value)

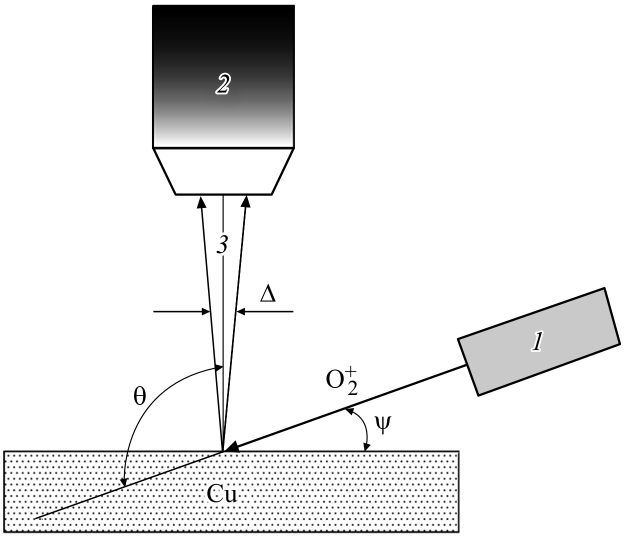

Figure 1. Schematic diagram of the experiment geometry: *1* — source of probing ions, *2* — mass–energy analyzer, *3* — beam of analyzed ions. The angle of incidence of the probing beam is $\psi = 30°$, the scattering angle is $\theta = 120°$, and the angle of entry of ions into the mass–energy analyzer is $\Delta \sim 10^{-4}$ sr.

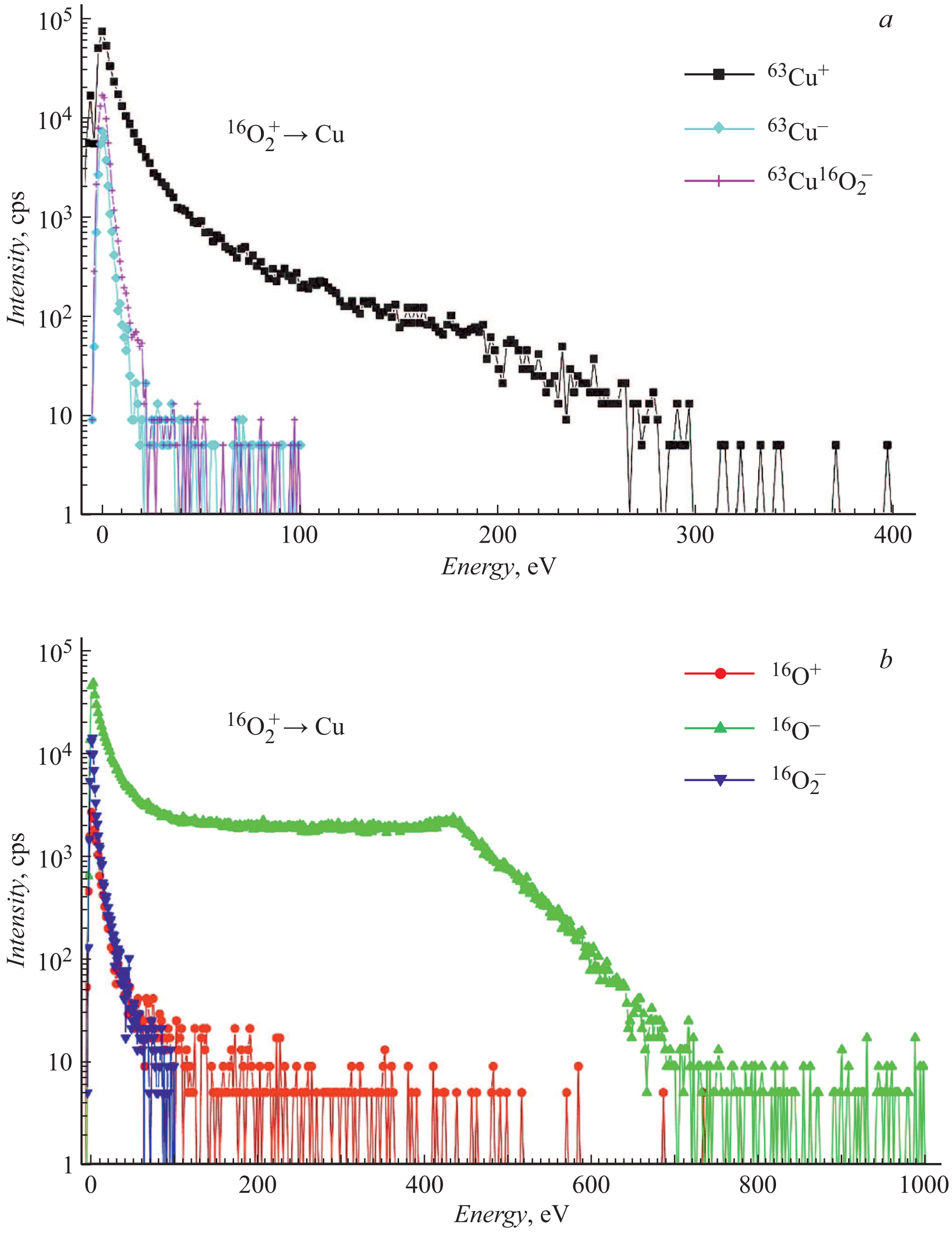

Figure 2. Energy spectra: *a* — sputtered ions containing copper; *b* — sputtered ($^{16}O^+$, $^{16}O^-$, and $^{16}O_2^-$) and scattered ($^{16}O^-$) oxygen ions.

for ions of both polarities within a narrow solid angle $\Delta \sim 10^{-4}$ sr with zero electric field in the space between the target surface and the input electrode of the mass–energy analyzer. The ion source was fitted with a Wien mass filter, and the focused beam of $^{16}O_2^+$ ions with a current density below $100\,\mu$A/cm^2 was scanned on the sample surface into a pattern $200 \times 200\,\mu$m in size. The angle of incidence of probing ions with respect to the sample surface (ψ) was 30°, and scattering angle θ (i.e., the angle between the direction of motion of bombarding ions and the mass–energy analyzer axis) was 120° (Fig. 1). Measurements were performed in steady-state conditions: the intensity of energy spectra did not depend on the bombardment time (bombarding ion dose). The vacuum in the analytical chamber during the measurements was no worse than 10^{-7} Pa.

Figure 2 presents the energy spectra of the most intense positive and negative secondary ions containing copper and oxygen in a semi-logarithmic scale. Note that the intensity scale in Fig. 2 has not been corrected for the difference in efficiency of detection of positive and negative ions by the secondary-electron multiplier. The maxima of all spectra in Fig. 2, *a* fell within the range of 1–3 eV; however, owing to the high intensity for $^{63}Cu^+$ ions, detector saturation and overload were apparent. As a result, a dip was observed at the peak of this spectrum. The spectrum of positively charged ^{63}Cu^{+} ions is a (quasi)classical spectrum of sputtered particles that can be characterized by the Thompson formula [9] within the model of linear cascades of elastic and inelastic collisions initiated by bombarding ions in the near-surface region of the target. Without getting into specifics of the processes of ionization of sputtered particles (see, e.g., [10] and references therein), it is fair to assume that the extended „tail" of this spectrum was formed due to the transfer of energy to sputtered copper particles from fast backscattered oxygen atoms/ions and direct-recoil copper atoms/ions. The spectra of negative atomic (^{63}Cu^{-}) and molecular (^{63}Cu^{16}O$_2^{-}$) ions presented in Fig. 2 differ from the spectrum of positive copper ions. They are narrower, and their intensity decreases to the level of noise of the secondary-electron multiplier at energies above 20 eV. It is highly likely that negative ions are produced due to the processes of electron exchange in a very thin layer of copper oxides that forms (regenerates) continuously on the target surface and is sputtered by bombarding oxygen ions. According to the SRIM-2008 data [11], the projected range for 1 keV ^{16}O ions (i.e., the depth at which the density of implanted oxygen ions in copper is maximized) is approximately 1 nm in the given experiment geometry. Since the electron affinity for copper is negative (-1.9 eV [12]), the process of production of negative copper ions should be endothermic (i.e., energy should be absorbed in this process) if no electropositive elements such as Cs, which may reduce the work function of the target material, are present on the copper surface.

Figure 2, *b* presents the energy spectra of atomic and molecular oxygen ions of both polarities. The spectrum of ^{16}O^{+} is close in shape to the ^{63}Cu^{-} spectrum; the differences are that it is broader (extends to energies on the order of $80-100$ eV) and its maximum is shifted toward higher energies ($\sim 8-10$ eV). The spectrum of negative molecular oxygen ions ^{16}O$_2^{-}$, which is presented in the same figure, also looks similar. It is likely that positive atomic and negative molecular oxygen ions are produced in the surface layer of copper oxides in the same way as negative copper and copper dioxide ions (see above).

The significant difference between the spectra of positive and negative atomic oxygen ions is noteworthy (Fig. 2, *b*). In our view, the energy spectrum of ^{16}O^{-} is a superposition of two spectra, namely the spectrum of sputtered oxygen ions with its maximum at energies around 10 eV and the spectrum of elastically and inelastically backscattered oxygen ions with its maximum at $450-460$ eV. The position of this maximum is able to estimate using the model of elastic binary collisions [2]:

$$E_1 = \left(\frac{\cos\theta + \sqrt{\alpha^2 - \sin^2\theta}}{1+\alpha} \right)^2 E_0 = K E_0, \qquad (1)$$

where E_0 and E_1 are the energies of bombarding and backscattered ions, respectively; $\alpha = M_1/M_0$ is the ratio of masses of a surface atom (Cu) and a primary ion (^{16}O); K is the kinetic factor. The kinetic factor in our experiment (at $\theta = 120°$ and $\alpha = 3.97$) is ~ 0.46. In the energy scale, this is roughly equivalent to the maximum of the energy spectrum of ^{16}O^{-} ions.

Thus, severa correlated processes proceed simultaneously when the surface of copper is bombarded with positively charged molecular oxygen ions: (1) sputtering of the target material that is accompanied by the emission of positively and negatively charged copper ions; (2) sputtering of oxygen-containing atoms and molecules from the surface ion-induced layer of copper oxides that is accompanied by the production of ions of both polarities; (3) intense elastic and inelastic scattering of bombarding oxygen ions that is accompanied by the processes of charge exchange (i.e., production of negative atomic oxygen ions owing to the possibility of multichannel capture of electrons from the valence band and the conduction band of copper). It should be noted that the scattering of positive oxygen ions has not been detected at the sensitivity level of our instruments.

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Conflict of interest

The authors declare that they have no conflict of interest.

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