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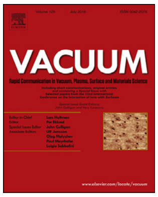

Inelastic processes in ion interaction with ZrO_2 surface

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ABSTRACT

Experimental studies and computer simulations of inelastic interaction of low-energy Ar^+ ions (100–2000 eV) with a ZrO_2 surface are presented. The experiments were performed using Auger electron spectroscopy and secondary ion mass spectrometry. It has been found that the change of surface composition and the intensities of sputtered Zr^+ and scattered Ar^+ ions depend non-monotonically on the incident ion energy. Moreover, Zr^+ and Ar^+ ion intensities oscillate in antiphase and correlate with the curve of the surface composition change. The results of computer simulations of the electron exchange between incident ion and surface atoms allow interpretation of the experimental data in terms of the quasi-resonant charge–exchange model.

1. Introduction

Oscillatory structure was observed for the first time in the case of low energy ion scattering from d-metal surfaces [1]. It was shown that the oscillatory dependence of scattered ion yield on the primary ion energy is attributed to quasi-resonant charge–exchange between the ion vacant level and the strong localized outer D-state of surface metal atom. Currently, significant progress is achieved in understanding the mechanisms of the electronic exchange between the incident ion and the surface of metals and semiconductors [2–13]. An understanding of these mechanisms is very important for a quantitative analysis of surfaces by low energy ion scattering [14].

On the other hand, in ion-covalent compounds such as metal oxides the charge transfer along a metal–oxygen bond results in essential localization of an electron at the oxygen atom. Therefore, a similar oscillatory structure was expected for the case of ion scattering from ion-covalent and ionic materials. Indeed, the oscillatory behavior was observed in scattering of Ar ions from a LiF surface [15], in sputtering of Sr^+ ion from $SrTiO_3$ surface under Ar^+ ion irradiation [16] and in the probability of the radiation defect generation in Al_2O_3 as a function of incident ion energy [17]. It was shown in Ref. [17] that resonant charge–exchange of Ar ions with the localized electron orbital of surface oxygen atom causes a decrease in the energy of Al–O bond, and consequently leads to formation of point defects in the crystal surface.

In work [18] Souda investigated the mechanism of secondary ions formation during He^+ bombardment of oxides. The O^+ ion desorption was observed only from a TiO_2 surface, while very little O^+ ejection occurred from MgO, Al_2O_3 and SiO_2 surfaces. Souda explained the O^+ emission from TiO_2 by strong valence orbital hybridization occurring in a strongly correlated system like transition-metal compounds which leads to the long-lived antibonding state with the O 2s core hole formed via the quasi-resonant charge–exchange with He 1s. Subsequent decay of the O 2s hole via the intra-atomic Auger process formed O^+ ions on the way out from the surface.

Sato et al. in Ref. [19] reported that sputtering yield of O^+ from the MgO surface caused by doubly charge Ar^{2+} irradiation was larger than that by Ar^+. They explained this charge dependence by suggesting that part of the O^+ produced by irradiation with Ar^{2+} was sputtered through the electronic processes. The O^+ ions are produced by the electron capture of Ar^{2+} and then they are desorbed from the surface by the Coulomb repulsion between the O^+ ions and their neighbors.

The study of chemical, compositional and electronic changes induced by 3 keV Ar^+ sputtering of ZrO_2 films has been carried out in works [20,21]. It has been found that Ar^+ bombardment induces electronic states in the band-gap region attributed to oxygen vacancies and changes in the O 2p valence band which are associated with the formation of a highly oxygen deficient surface layer due to preferential sputtering of the oxygen atoms.

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In this paper we report the experimental results on inelastic interaction of argon ions in the energy range 100–2000 eV with the surface of a ZrO_2 single crystal as well as their theoretical analysis using computer simulation of electron exchange between an incident ion and surface atoms.

Zirconia (ZrO_2) is of great interest due to its outstanding properties such as high dielectric constant ($\varepsilon = 25$), wide band gap (>5 eV), high chemical and thermal stabilities, low optical loss and high transparency in the visible and near-infra-red regions [22,23]. This material is used for applications in gas sensors, fuel cells, catalysis, high-index films, high durability coatings and ceramics. At present, ZrO_2 is extensively studied as an alternative gate dielectric which is being considered to replace SiO_2 [24]. It can also be used as an insulator in the storage capacitor of a dynamic random access memory and in the flash memory cells.

2. Experiments

All experiments have been performed in a standard UHV chamber with a base pressure below 10^{-9} mbar, equipped with an Auger electron spectrometer, a quadrupole mass spectrometer and an ion gun.

In our experiments we used a single crystal of yttria-stabilized cubic zirconia. Cubic zirconia has the ideal calcium fluorite structure with lattice parameter of 0.517 nm. The zirconium atoms are situated in an fcc lattice, i.e. at the corners of the cubic elementary cell as well as at the halves of the <110 > directions. Oxygen atoms lie at the quarters of <111 > directions.

The surface of a ZrO_2 single crystal was cleaned outside of the vacuum chamber by heating for 1 h in an O_2 atmosphere at the temperature of 900 °C. It was then introduced into the UHV chamber without contacting the atmosphere. After such a treatment Auger spectroscopy revealed the absence of any contamination at the surface.

The investigation of the modification of the ZrO_2 single crystal surface under low energy Ar ion irradiation was performed by the method of Auger electron spectroscopy. After irradiation with a dose of 10^{18} cm^{-2} the Auger peaks of metal and oxygen were recorded in the differential form. The spectra obtained were smoothed, integrated and background subtracted according to the original [25] and usual procedures. Then the areas of the Auger peaks of metal (I_{Zr}) and oxygen (I_O) were calculated. The ratio I_{Zr}/I_O measured for the irradiated surface characterizes the deviation x from the surface stoichiometry. Assuming the ratio for a non-irradiated (stoichiometric) surface is equal to 1, we determined the deviation x by the formula $x = I_{Zr}/I_O - 1$.

After irradiation and recording of the spectra, the sample was annealed in vacuum for 30 min at the temperature of 700 °C until the ratio I_{Zr}/I_O corresponded to that for a non-irradiated surface. Under these annealing conditions the Ar ion-induced oxygen vacancies were replaced by oxygen interstitials diffusing to the surface from the bulk of the crystal.

A quadrupole mass spectrometer (QMS) was used to detect the reflected and sputtered ions. The angle between the low-energy ion beam and the axis of QMS was 90°. The incidence angle of ions at the target was 45°. A specially designed ion gun with an energy distribution half-width of less than 5 eV was used. The primary ion energy was varied in the range from 100 to 2000 eV by steps of 100 eV. The ion current density was 10 $\mu A/cm^2$.

3. Calculation model

In this study, we calculated the electron exchange between the vacant orbital of the incident ion and the surface using the time-dependent Andersen-Newns (TDAN) model [26]. The trajectory of the ions is determined by interaction simultaneously with a set of surface atoms located in the two top layers. The Born-Mayer interatomic interaction potential $U(R)=A_{BM}\exp[-B_{BM}R]$ was used. Here, R is the distance between the interacting particles, A_{BM} and B_{BM} are the Born-Mayer coupling constants [27].

We used this model for the first time in work [17] for calculation of the probability of Ar^+ ion neutralization on the surface of Al_2O_3. In these calculations the exchange potential was taken in the form $V(t)=V_0\exp(-r(t)/R_0)$, where V_0 is the interaction magnitude and R_0 is the typical distance of charge–exchange.

Afterward, it has been shown [16] that for adequate description of charge–exchange processes it is necessary to consider the hybridization of the ion and surface-atom orbitals, since the interaction potential is determined by the overlap of their corresponding wave-functions.

A new approach was based on the numerical calculation of the charge–exchange using a hopping integral approximated by the Gaussian function:

$$V_i(t) = V_0 \exp\left[-\frac{(r_i(t)-r_0)^2}{b^2}\right],$$

where V_0 (interaction constant) and b (parameter describing the atomic orbital broadening) were taken from the tables of interatomic matrix elements for 3p Ar – 2p O and 3p Ar – 4p Zr, calculated by the Hartree-Fock method [28], r_0 is a fitting parameter, $r_i(t)$ is the distance between the ion and the corresponding surface atom.

This approach was further developed in Ref. [15] where a new model of ion neutralization, based on the two different positions of the ion orbitals with different orientations, was proposed. We used this model in our present work.

4. Results and discussion

ZrO_2 surface composition changes induced by the low energy Ar ion bombardment were measured by using Auger electron spectroscopy.

Fig. 1 shows the dependence of the deviation x from the zirconia surface stoichiometry on the energy of irradiating ions. One can see that the irradiation of the surface with argon ions leads to the damage of the essentially anion sub-lattice. The preferential sputtering of oxygen is associated with the large difference between the oxygen and zirconium surface binding energies estimated by Kelly for ZrO_2 [29]. The zirconium surface enrichment increases with an

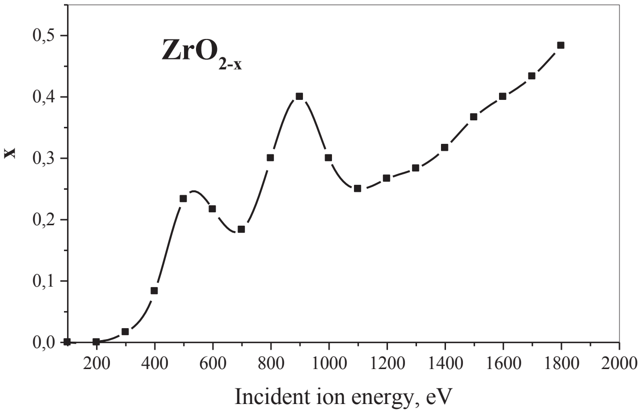

Fig. 1. Dependence of deviation from the stoichiometric composition x at ZrO_{2-x} surface on energy of irradiating Ar^+ ions.