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Electron-stimulated positive ion emission from NaCl crystal surface

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Abstract

The energy and the mass distributions of positive ions emitted from the surface of ultrathin epitaxial NaCl films under 1–5 keV electron beam have been measured. Two peaks in the energy spectra have been found. The low energy one, composed mostly of Na^+, Cl^+ and Cl_2^+ ions, is temperature dependent, and scales quadratically with the electron current. This peak clearly corresponds to the gas-phase ionisation of neutral atoms. The second, with a maximum around 1 eV, is composed exclusively of Na^+ ions, does not depend significantly on the crystal temperature, and scales linearly with the electron current. This last peak seems to be due to ions ejected from the crystal surface as a result of the Coulomb instability. Depending on the crystal temperature and the electron current density either the first or the second component may become dominating, explaining the discrepancies in results obtained so far by different authors.

1. Introduction

Electron stimulated emission of ions from ionic insulators has been a matter of wide interest since Knotek and Feibelmann [1] presented the evidence for the Coulomb instability driven emission of positive ions from ionic oxides. Further investigations carried out by Pian et al. [2] revealed that also electron bombarded alkali halides emitted positive ions which was believed to be due to the Knotek and Feibelmann mechanism. On the contrary, molecular dynamics calculations by Walkup and Avouris [3] and their experimental work [4] showed that radiation induced Coulomb instability mechanism might not be effective for alkali halide ionic crystals. Instead, they proposed that neutral atoms emitted as a result of crystal radiolysis [5] are ionised in the vacuum out of the sample by secondary electrons. They argued that after the halogen ion charge reversal, within 15–30 fs initial repulsive configuration was rapidly lost through the rearrangement of the neighbouring ions and the halogen particle was retrapped at the surface. Moreover, their experimental results showed the quadratic dependence of ion yield on a primary electron current and virtually identical mass spectra of ions and neutrals emitted from sodium chloride crystal. In conclusion they discarded Knotek–Feibelmann model in case of alkali halide ionic crystals. More recent calculations by Green, Riley and Coltrin [6] basically gave the same results.

2. Experimental

The experimental apparatus consisted of two chambers. The preparation chamber was designed for the substrate cleaning and thin alkali halide film deposition in the molecular beam epitaxy process. It contained the ion gun for sputter cleaning of gallium arsenide substrate, sample holder fitted with an oven for sample annealing, a Knudsen effusion cell and a quartz crystal microbalance for the film thickness controlling, with a fraction of monolayer accuracy. The analysis chamber was equipped with a LEED diffractometer, a hemispherical energy analyser, an electron gun, and a quadrupole mass spectrometer. It also contained the sample holder the same as in preparation chamber and the sample could be moved between the holders by means of the magnetically coupled transfer. The base pressures were $< 5 \times 10^{-10}$ and $< 5 \times 10^{-9}$ Torr in the analysis and the preparation chambers respectively. A detailed description of the film preparation procedure will be published elsewhere [7]. Thin (100–1000 Å) sodium chloride films were deposited on gallium arsenide (100) surface. Such thin layers allowed measurements for which sample charging is dramatically reduced in comparison with the bulk NaCl target. The following dependences were determined in these experiments: energy spectra of ions emitted from the films versus sample temperature and primary electron current, mass spectra of emitted ions, and time-of-flight distributions for selected ion energies. The sample temperature was varied in the range 90–250°C which prevented the surface stoichiometry changes [8]. There was a considerable temperature uncertainty (< 20%) as the thermocouple was attached to the sample holder far

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from the sample and there were a few thermal contacts which could be bad. The primary electron current was in the range of 0.02–1.3 μA and most measurements were done at the electron energy of 1 keV although there were also runs at 0.1, 3 and 5 keV. The beam was focused into a spot of approx. 0.5 mm in diameter and scanned over the area 5 mm × 5 mm in order to avoid thin film erosion. The desorption rate could be estimated as ~ 0.25 monolayer μA s [7]. Time needed to measure single spectrum was ~ 10 s. During the energy spectra recording the sample was biased with + 1 to + 6 V potential in order to improve the energy analyser transmission.

3. Results and discussion

An example of the energy spectra of ions emitted from NaCl film is presented in Fig. 1. The spectra were taken from 100 Å film at the elevated sample temperature and with low electron current. These conditions allowed the sample charging minimization. It can be seen that the spectra have two components: the first narrow low energy peak and the second much wider peak with a maximum at energy higher by ~ 0.8 eV. The spectrum obtained with a higher current is slightly shifted to the right which indicates the "positive" charging of the sample. Similar spectra have been obtained also at different energies and for different film thicknesses. In these cases the peaks were, however, considerably broadened and shifted due to more severe charging.

The set of ion energy spectra taken for different sample temperatures is shown in Fig. 2a, and the integrated intensity of the two spectrum components taken as the area under each of the two peaks is plotted in Fig. 2b. Within the investigated temperature range the first peak dramatically increases with increasing temperature while the second peak stays constant.

It is well established that alkali halide crystals irradiated with energetic electrons predominantly emit alkali and halogen atoms. Alkali atoms always have thermal energies while halogens for some crystals have two component velocity spectra and in addition to the "thermal" atoms a nonthermal component is present [9]. The "thermal" atom emission has activation type temperature dependence, whereas the "nonthermal" emission decreases with increasing temperature although the dependence is much weaker [10]. Taking into account Walkup and Avouris results [4] and their estimation that the fraction of emitted ions equals roughly to ~ 10^{-6}, in a good agreement with post-ionisation probability, one could argue that our two component ion energy spectrum simply reflects the two component energy spectrum of primarily emitted neutrals ionised in vacuum by secondary electrons. However, in the case of sodium chloride, always a single component velocity spectrum ("thermal" particles only) was observed. Nevertheless, the lower energy peak may have post-ionisation origin. Further evidence for such interpretation comes from the primary electron current dependence of ion emission which is plotted in Figs. 3a and 3b. The first component intensity scales quadratically with electron current which indicates that those ions are produced in the second order process which we may attribute to emission of neutral atoms and their ionisation by secondary electrons. The second peak is found to scale linearly with the electron current (see also the best fits – solid lines in Fig. 3b).

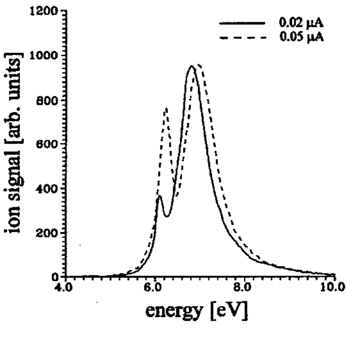

Fig. 1. Energy spectra of ions emitted under 1 keV electron beam from (100) NaCl surface for two different primary electron currents. The spectra are normalised to the maximum. Sample temperature: ~ 250°C, bias voltage: + 5 V.

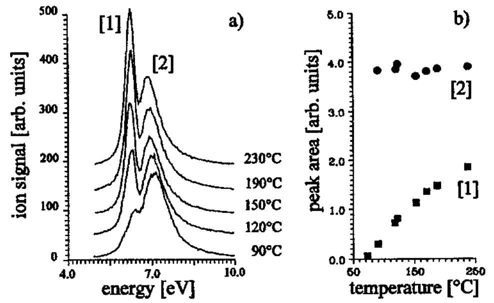

Fig. 2. A set of the energy spectra for few different temperatures (bias voltage + 5 V) (a) and the peak areas vs. sample temperature (b).

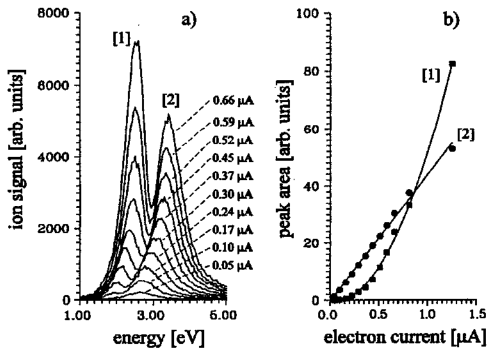

Fig. 3. A set of the energy spectra for few different currents (a), and the peak areas vs. primary electron current (b). Sample temperature: 175°C, bias voltage 1 V.

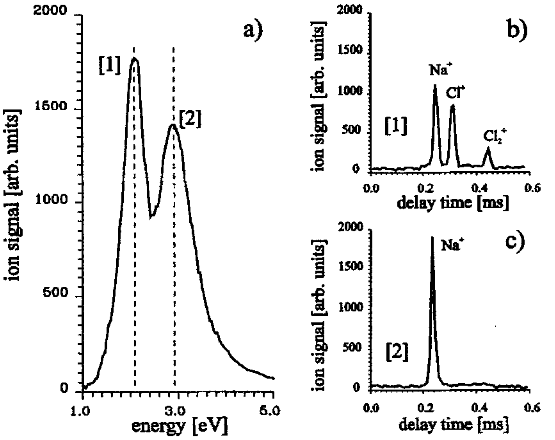

Fig. 4. The energy spectrum of ions emitted from (100) NaCl (a) and the TOF spectra of the two components (b) and (c). Dashed lines at ~ 2.1 and ~ 2.9 eV denote points at which spectra b and c, respectively, were recorded. Sample temperature: 200°C, bias voltage: 1 V.

In order to determine the mass of the emitted ions two types of measurements have been performed. Initially a quadrupole mass spectrometer was used. The spectra taken with high electron current (about 5 μA) were virtually identical both for emitted ions and neutrals which was a repetition of Walkup and Avouris result [4]. More decisive measurements were performed by combining our energy analyser with a high performance correlation time-of-flight electronics. In Fig. 4a we show the energy distribution of ions emitted from a 200 Å thick NaCl film desorbed with a 1 keV electron energy and 0.25 μA current. The analyser transmission energy was fixed at the peak maxima (2.1 and 2.9 eV) and subsequently time-of-flight distributions through the energy analyser were measured. They are presented in Figs. 4b and 4c. The first peak of the energy spectrum is composed of ions of three different masses. It is somewhat difficult to determine the mass scale directly as the analyser together with a focusing column makes rather complex electrostatic system. Nevertheless, if we assume that the first peak is due to mass 23 (Na^+) we find the second and the third peaks centered at mass 35.5 (unresolved masses 35 and 37 of Cl^+ isotopes) and at mass 71.3 (unresolved masses 70, 72, 74 of Cl_2^+), respectively. This makes the picture consistent with a quadrupole mass spectrometer result for high current conditions where similar mass spectrum was observed [4]. The second peak of the ion energy spectrum is composed exclusively of Na^+ ions.

Now it seems quite clear that the first low energy peak which is narrow, goes up with temperature, scales quadratically with the electron current, and its mass spectrum is identical with that of neutral atom electron stimulated emission, is determined by the gas-phase ionisation. Consequently the ions corresponding to this peak must be emitted from crystal with energies in the range 0.05–0.1 eV. However, this energy is afterwards changed by the bias voltage, contact potentials and sample charging. The second peak which has corrected maximum at about 0.9 eV, and which does not depend significantly on the crystal temperature and scales linearly with the electron current is most probably due to the Coulomb instability of the crystal lattice following halogen ion charge reversal below the surface sodium atom.

Our results confirm the theoretical predictions by Elango et al. [11] and by Walkup and Avouris [3]. They found that halogen ions cannot be ejected from the ionic rocksalt lattice after their charge reversal. The positive ion ejection may occur, however, if the charge reversal takes place on a halogen atom below the surface alkali ion or below the alkali ion in the surface adatom site. Our results provide the first direct experimental evidence that the positive alkali ion emission can take place in alkali halides due to specific surface mechanism induced by electronic transitions.

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