

Ground-State and Excited Atom Production by Electron and Ion Bombardment of NaCl and CaF₂

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1. Introduction

For alkali and alkali earth halides, ion, electron and photon bombardment are efficient processes leading to continuous surface erosion [1,2]. While sputtering of metals under ion bombardment is well understood in terms of a collision cascade emission mechanism based on momentum transfer due to elastic collisions [3], for electron or photon bombardment no such processes can account for any particle emission due to the negligible momentum transfer. Electronic processes have been proposed to explain such electron or photon induced desorption processes [4,5]. Selective emission of the halogen atoms and molecules is ascribed to the H-centre migration model leading to the formation of a metal overlayer on the surface. If the vapour pressure of the alkali/alkali earth metal layer at the target temperature is high enough these excess metal atoms will desorb thermally, thus leading to continuous particle emission. Otherwise the excess metal layer will eventually prevent any further halogen emission and the emission process will be only of transient nature [6]. We have compared the particle emission processes for ion and electron bombardment of NaCl and CaF₂ to differentiate between a collision cascade induced contribution and one due to Desorption Induced by Electronic Transitions (DIET) under ion bombardment and, in addition, to compare DIET processes under ion and electron bombardment to obtain a better understanding of the desorption mechanisms involved.

Even though emission of ions, excited and ground-state metal atoms has been observed, evidence exists that the majority of electronically desorbed particles are neutral ground-state atoms [7]. Using high resolution optical spectroscopy [8] and Laser Induced Fluorescence spectroscopy (LIF) [9] we have studied the energy distributions of ground-state as well as of excited Na and Ca atoms at different target temperatures. In addition the yield - temperature dependence for ground-state and excited atoms was studied to gain insight on whether excited atoms are formed by an intrinsic process at the surface or by post-excitation of emitted ground-state atoms in the gas phase due to secondary electrons or the primary electron beam.

2. The velocity distribution of ground-state Na and Ca atoms under ion and electron bombardment

LIF, employing the Doppler effect, was used to measure the velocity distribution of emitted Na/Ca atoms from NaCl/CaF₂ single crystals under 15 keV Ar ion (current

density $5\mu\text{A}/\text{cm}^2$) or 400 eV electron (current density $200\mu\text{A}/\text{cm}^2$) bombardment in the temperature range from 300 to 700 K. In the case of Na, in essence, the velocity distribution was found to be identical for electron and ion bombardment at all temperatures within the accuracy of our measurements (see Fig. 1) and, in addition, the distribution was purely thermal and could always be fitted with a Maxwell-Boltzmann distribution at target temperature. No cascade contribution was resolved (which should exhibit a maximum at much higher energies around 0.5 eV, which is half the binding energy for Na [10]).

To check for the absence of any cascade contribution under ion bombardment of a clean NaCl target further experiments showed that if the oxygen partial pressure in the vacuum chamber is increased up to 10^{-6} mbar the sputtered thermal Na flux decreases by about a factor of 5 and in addition a non-thermal cascade contribution now becomes evident.

On the other hand, in the case of ion bombardment of CaF_2 at room temperature and up to 500K the velocity distribution is purely collisional and a fit of the distribution using the Thompson formula [3] for metals gives a surface binding energy of 1.4 eV, in perfect agreement with previous measurements, we have performed for metallic Ca [11]. Starting with temperatures above 500K, an additional thermal component appears in the energy distribution, and for temperatures above 600K this becomes the dominant contribution to the sputtered flux (Fig. 2). The differences between the velocity distributions for Na and Ca under ion bombardment can be easily explained in terms of the much higher vapour pressure of Na. Thus we assume that for NaCl already at room temperature the thermal component is so dominant that the cascade contribution could not be resolved.

For both materials under ion bombardment the thermal component in the emitted flux is ion beam induced and not a pure thermal evaporation, as was confirmed by chopping the ion beam. In addition, for ground-state Ca emission from CaF_2 we investigated the time dependence of the LIF signal in more detail. As can be seen from Fig. 3, at least three different contributions to the sputtered flux can be identified for temperatures above 500K:

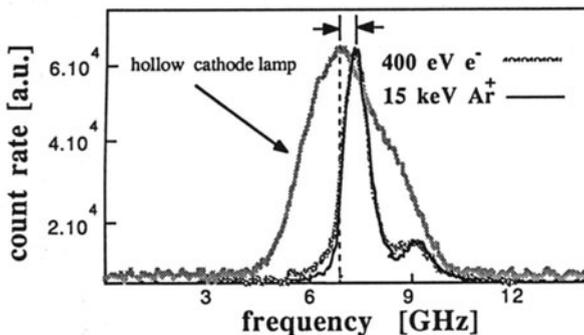


Fig.1: LIF spectra over the velocity distribution of emitted ground-state Na atoms under ion or electron bombardment. The spectra are identical within the accuracy of the measurements. The frequency shift between the maxima of the hollow cathode lamp and the fluorescence yield curves corresponds to 320K, which was the actual target temperature. Any energetic cascade contribution under ion bombardment should be visible as a tail towards higher frequencies.

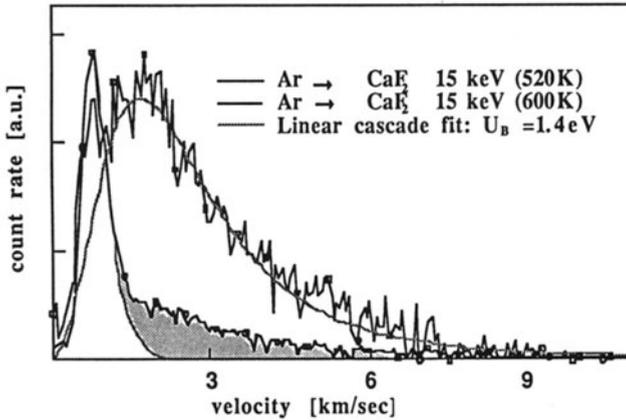


Fig.2: Normalized velocity spectra of ground-state Ca atoms under 15 keV Ar ion bombardment. At 520K the spectrum is mainly collisional and can be fitted by the linear cascade theory assuming a surface binding energy of 1.4 eV. At 600K the spectrum is mainly thermal and the cascade contribution is visible only as a tail in the distribution (shaded area). The thermal part of the spectrum corresponds to a Maxwell-Boltzmann distribution at target temperature.

- a) A **prompt decrease** of the signal by almost an order of magnitude was observed immediately after the ion beam was removed from the target (Fig.3, target temperature 600K). Due to the limited time resolution we only know that the decrease is faster than 0.1 s. As at 600K the thermal contribution is dominant (more than 90%), we assume that these promptly emitted atoms consist in reality of two contributions: the **cascade** contribution at non-thermal energies which should not last longer than 10^{-12} - 10^{-11} s [12] after the ion bombardment is stopped and a **thermal** contribution due to V_k centres. These V_k centres cause emission of the halogen atoms and as a consequence evaporation from a Na-enriched surface occurs. As the lifetime of these V_k centres is of the order of milliseconds they will also contribute to the prompt decrease [4].
- b) A **slow thermal contribution** exhibiting a life time of the order of 30 s, which we assume to be caused by long-lived trapped exciton states diffusing to the surface and in turn causing Na emission similar to the V_k centres.
- c) A **purely thermal evaporation** component, not caused by ion bombardment, which is for the whole temperature range investigated a minor contribution to the sputtered flux.

Under electron bombardment CaF_2 showed no emission of Ca ground-state atoms up to 500K, the same temperature for which under ion bombardment a thermal contribution appeared. At temperatures above 500K as outlined above pure thermal evaporation occurs and in addition under electron bombardment Ca desorption (signal size under our experimental conditions about 4 times the thermal evaporation at 550K) occurred. After turning off the electron beam a delayed signal with a decay time constant of the order of 3 min was observed in this case (target temperature 550K), possibly indicating that under electron bombardment either other long-lived excitons are created or that the different decay time as compared to

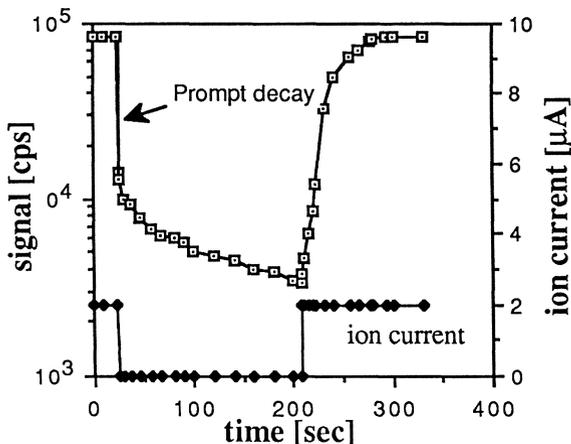


Fig.3: Time dependence of the Ca ground-state signal if ion bombardment is interrupted at a target temperature of 600K. The fully drawn part of the curve labelled "prompt decay" corresponds to a signal decrease within less than 0.1s.

ion bombardment is caused by the greater penetration depth of the primary electrons. In all cases under electron bombardment the velocity distribution was thermal, corresponding to a temperature equal to the target temperature.

3. Energy distribution of excited Na and Ca atoms under electron and ion bombardment

To determine which process causes emission of excited Na and Ca atoms, we measured the energy distribution of excited Na (Na I 588.9nm) and Ca (Ca I 422.5nm) atoms using high-resolution optical spectroscopy studying the Doppler line profile broadening [8] of the cited lines. For NaCl under ion as well as electron bombardment strong optical emission is observed and the analysis shows that under ion bombardment excited atoms are non-thermal, exhibiting an energy distribution which peaks at about 3 eV. Contrary to this, under electron bombardment a thermal distribution was found for the Na I atoms [9]. These results are in good agreement with measurements by WALKUP et al. [13], who using a similar technique obtained the same results. The high energies of excited atoms under ion bombardment indicate that these atoms are part of the cascade contribution being excited when leaving the surface during the last collision.

In the case of Ca I from CaF₂ under ion but not under electron bombardment emission of excited atoms was observed over the whole temperature range investigated. For ion bombardment the velocity distribution of Ca I was identical to the emission from a pure Ca target, and a mean energy of 6 eV was derived from the analysis [8].

4. The dependence of the yield of ground-state and excited atoms on the target temperature

To gain additional information on whether excited atoms under electron bombardment are caused by secondary effects (excitation by secondary or primary electrons) [1,13] or due to an intrinsic process [14], we studied the temperature dependence of the yields by LIF or light emission, respectively. Figure 4 a,b give the results for

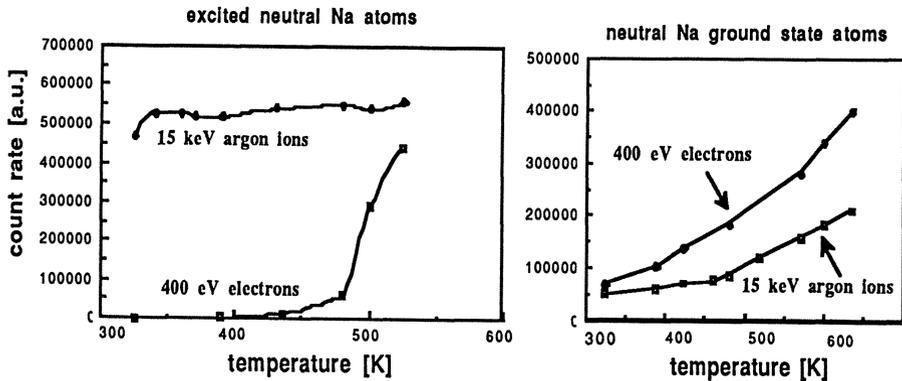


Fig.4: Temperature dependence of the Na ground- and excited-state yields, under ion or electron bombardment.

NaCl, which clearly show that under electron bombardment the excited yield is proportional to the ground-state yield and both increase exponentially with temperature. However, under ion bombardment only the ground-state yield shows a significant dependence on temperature. The independence of the yield of excited atoms with temperature and their non-thermal energies strongly suggest their origin from the collision cascade. The increase in the ground-state yield follows from the observation that the majority of emitted Na atoms are thermal and caused by thermal evaporation following electronic desorption of the halogen atoms. The results for electron bombardment together with the thermal energy distribution of the excited atoms do not contradict a formation mechanism due to gas phase collisions. However, the absence of any excited Ca atoms under electron bombardment of CaF₂ contradicts the assumption of gas phase collisions and indicates other processes causing the emission of excited atoms.

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References

1. Z. Postawa, J. Rutkowski, A. Poradzisz, P. Czuba, M. Szymonski: Nucl. Instr. Meth **B18**, 574 (1987)
2. R.F. Haglund Jr., N.H. Tolk, G.M. Loubriel, R.A. Rosenberg: Nucl. Instr. Meth. **B18**, 549 (1987)
3. P. Sigmund: Phys. Rev. **184**, 383 (1969)
4. P.D. Townsend: Nucl. Instr. Meth. **198**, 9 (1982)
5. N. Itho: Nucl. Instr. Meth. **B27**, 155 (1987)
6. R. Kelly: Surface Science **90**, 280 (1979)
7. N.H. Tolk, P. Bucksbaum, N. Gershenfeld, J.S. Kraus, R.J. Morris, D.E. Murnick, J.C. Tully, R.R. Daniels, G. Margaritondo, N.G. Stoffel: Nucl. Instr. Meth. **B2**, 457 (1984)
8. G. Betz: Nucl. Instr. Meth. **B27**, 104 (1987)
9. W. Husinsky, G. Betz: Scanning Microscopy **1**, 1603 (1987)
10. W. Husinsky, R. Bruckmüller: Surface Science **80**, 637 (1979)

11. W. Husinsky, I. Girgis, G. Betz: J. Vac. Sci. Techn. B3.5, 1543 (1985)
12. R. Kelly: Radiat. Effects 80, 273 (1984)
13. R.E. Walkup, Ph. Avouris, A.P. Gosh: Phys. Rev. Lett. 57, 2227 (1986)
14. R.F. Haglund Jr., R.G. Albridge, D.W. Cherry, R.K. Cole, M.H. Mendenhall, W.C.B. Peatman, N.H. Tolk, D. Niles, G. Margaritondo, N.G. Stoffel, E. Taglauer: Nucl. Instr. Meth. B13, 525 (1986)