Kinetic electron emission in the interactions of slow ions with MgO surfaces

P. Riccardi a,b,*, P. Barone a, A. Bonanno a, A. Oliva a, P. Vetrò a, M. Ishimoto b,c, R.A. Baragiola b

a Laboratorio IIS, Dipartimento di Fisica, Università della Calabria, and INFN Unità di Cosenza, 87036 Arcavacata di Rende, Cosenza, Italy
b Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA 22904, USA
c Fujitsu Laboratories Ltd., Akashi, Hyougo 674-8555, Japan

Abstract

We report experimental energy distributions and yields of electrons emitted from MgO surfaces under the impact of slow noble gas and sodium singly charged ions at varying incident energies.

At impact energies below ~1 keV, electron spectra are nearly independent of ion type and energy. A tail of high-energy electrons is observed to grow at higher impact energies.

The results are explained in terms of promotion of oxygen-2p electrons during binary projectile-oxygen collisions populating continuum and excitonic states. Excitons can significantly contribute to electron emission due to the negative electron affinity of the surface.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Ion-induced electron emission from solids is due to the two main processes of potential and kinetic electron emission [1,2]. In potential electron emission, electron excitation results from the conversion via Auger processes of the potential energy carried by the incoming ions when they are neutralized by electron capture from the surface. In kinetic electron emission, excitation results from the transfer of kinetic energy of the incoming ion.

These excitation mechanisms have been extensively studied using metal target, while insulator materials received considerable less attention, due to experimental difficulties arising because the surface charges up during ion bombardment.

Among the insulator materials which are currently the subject of an intense scrutiny, magnesium oxide is one of the most interesting. This is
because it is a prototypical ionic insulator and because of advantageous properties of this material for use in plasma display panels: a large ion induced electron yield (and therefore a low discharge voltage) and high stability under ion bombardment.

Experiments of electron emission from MgO samples by slow ions have been recently reported by us and other groups [3–7]. A consistent observation reported in many of this works is that the energy distributions of emitted electrons resulted independent on the type of projectiles.

Different interpretation were proposed to explain this remarkable finding such as Auger neutralization (AN) [1] of incoming ions, whose ionization potential is shifted in front of the crystal surface [4], or decay of collisionally-excited (MgO) pair [7]. Thus, the important question that has to be answered is whether the excitation mechanism is driven by the potential or by the kinetic energy of incoming projectiles.

In this work, we extend our measurements of energy distribution of electrons emitted from MgO surfaces by slow ions to higher impact energies than those used in previous research [4]. We observe that electron spectra do not change at impact energies below \( \sim 1 \text{ keV} \) and are very similar for different projectile ions.

At higher impact energies, spectra of electrons emitted by He\(^+\), Ne\(^+\), Na\(^+\) and Ar\(^+\) ion bombardment broaden due the growth of a continuous tail of high-energy electrons.

The results are consistent with a recently proposed model [4] in which excitation occurs when oxygen-2p electrons are promoted during binary projectile-oxygen collisions to continuum and excitonic states. Excitons can decay into vacuum due to the negative electron affinity of the MgO surface.

### 2. Experiments

The experiments were performed in UHV (\( \sim 10^{-10} \) Torr) using a double pass cylindrical mirror energy spectrometer. The spectrometer was operated at constant pass energy of 50 eV and a resolution of 0.2 eV.

The surface of the samples was normal to the ion beam and electrons were collected at angle of 78° with respect to surface normal.

Sodium ions were produced in thermal ionization source. Noble gas ions were produced in an electron impact source, which was operated at electron energy of 58 eV. Measurements performed at an electron energy of 30 eV in the ion source showed that contamination of the ion beam with doubly charged ions was negligible.

MgO samples were prepared by electron beam deposition on a highly doped Si substrate and their thickness was approximately 100 nm. They were polycrystalline with the grains oriented such that they present an oxygen terminated (111) surface, as determined by X-ray diffraction. Samples were sputter cleaned for about 1 h by 1 keV Ar\(^+\) ion bombardment at a current density of 5 \( \mu \text{A/cm}^2 \) and the cleaning was monitored by Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS). Weak features due to band-gap states appeared in the EELS spectra before cleaning [8]. AES and EELS spectra for the sputter cleaned MgO surfaces were in excellent agreement with well-known spectra reported in literature [9–11]. Distortion of the electron energy distributions due to surface charging was prevented by neutralizing the positively charged sample with an electron flood gun right before the measurements. The energy of the Auger transition observed in the AES spectra after this procedure ensured neutrality of the sample.

The ion-induced spectra were acquired with the sample biased at a negative voltage \( V_b = -4.9 \text{ V} \). During the acquisition of the ion induced spectra, the ion current density was kept in the range of \( 10^{-1} \mu \text{A/cm}^2 \) and the acquisition time was \( \sim 20 \) s. Repeated acquisitions showed that surface charging and damage had no significant effects over this time interval.

### 3. Results and discussion

Fig. 1 reports electron emission yields \( \gamma \) for He\(^+\), Ne\(^+\), Na\(^+\) and Ar\(^+\) ion bombardment of MgO surfaces as a function of incident ion energy. These yields were obtained from the current mea-
sured on the sample under positive and negative bias, with an uncertainty of ~30%.

Fig. 2 shows energy distributions of electrons emitted by 500 eV Ne⁺ and Na⁺ impact. The spectra have been normalized to the same height to compare line shapes. Fig. 2 shows a remarkable finding of our investigations: at low impact energies, the shape of the energy distributions is nearly the same for different ions. This result is consistent with experiments of electron emission from MgO surfaces by slow ions, recently reported by us [3,4] and other groups [5,7]. On the other hand, as discussed in [4], charging of the surface during ion impact can explain inconsistent results reported in [6].

The very similar electron energy distributions and yields measured for Na⁺ and Ne⁺ projectiles is a strong argument against the idea that Auger neutralization (AN) dominates electron emission from MgO, which has been often invoked in previous works [4,6,12]. The fact, that electron spectra do not depend on the ionization energy of incoming projectiles, strongly suggests that electron emission is due to decay of some excited state intrinsic to the solid (i.e. not involving the electronic properties of the projectiles) populated by the transfer of kinetic energy of incoming ions.

In previous research [4], we have shown that this results are consistent with a model in which excitation occurs by electron promotion, when the valence shell of the projectile and the oxygen anion interpenetrate during a close atomic collision, forming a transient “quasi” molecule. Collisions with oxygen anions promote oxygen-2p electrons along quasi-molecular orbitals (MOs), above a threshold projectile energy which has been determined to be ~50 eV for the analogous case of Na⁺ exciting oxidized Al [13]. The O-2p electrons can be promoted by all the projectiles studied, as follows from calculations for these and similar systems [14,15], and from Barat–Lichten MO correlation rules [16]. The promoted MO are 3d⁺(He–O), 3p⁺ and 4f⁺(Ne–O, Na–O) and 4f⁺(Ar–O). The promoted MO cross-empty levels, such as the 3s, 4s for He, Ne and Na projectiles and the 3d, 4s for Ar, correlating with O-3s and O-4s excitons.

We have proposed that excitons can decay into vacuum and thus contribute to electron emission. Excitons are normally considered to be bound states of solids but, in MgO (and in LiF), the negative electron affinity of the surface causes the exciton to be above the vacuum level [17]. The band gap of MgO (7.8 eV in the bulk) drops at the
surface due to the decrease in the Madelung potential, by more than 1 eV, with variations among different crystal faces [18,19]. There is also a decrease in the exciton energy from a bulk value of 7.7 eV to a value which, for MgO(100), is 6.2 eV from high resolution EELS measurements [17]. The surface exciton exists in a region of changing surface potential, extending from outside the solid to the first atomic layers. To establish the position of the vacuum level, we determined the ionization energy of our samples (energy difference between the top of the valence band and the vacuum level) by measuring the photoelectron threshold [4]. The value of ~5.3 eV is consistent with the minimum energy loss measured in EELS [17] and with calculations [19]. The negative electron affinity of the surface (vacuum level below the conduction band minimum in the bulk) allows excitons to couple to the continuum of states outside the solid, which may contribute to the considerable width of surface excitons [17].

To gain further insight into the electron excitation mechanisms, we measured electron spectra for Ar+ and He+ impact, at varying incident energies. The spectra are reported in Figs. 3 and 4. We note that the shape of the distribution do not change for low impact energies, further reinforcing the idea of the preferential excitation of a state intrinsic to the solid.

On the other hand, a tail of high-energy electrons is observed to grow at higher projectile energy and is enhanced for faster He ions. To explain this observation, we consider that, once promoted, the O-2p electrons can transfer to excited states at the crossings of the promoted MO with unfilled MOs that correlate to excitons and conduction band states. The population of the final levels will decrease with excitation energy ΔE, and therefore will favor excitonic to continuum states. The probability for direct excitation to continuum states falls exponentially with the ratio ΔEv, where v is the relative collision velocity [20]. We attribute the cause of the high-energy tails in the spectra to those direct excitations, since these tails decay near exponentially and are enhanced for faster projectiles. This interpretation of the high-energy tail is analogous to that used to discuss similar experiments on LiF [21,22]. We differ, however, in the identification of electronic states responsible for electron emission. For LiF
it has been proposed that electron promotion leads to an autoionizing doubly excited atomic state \(F^{-}\) (2p\(^4\)3s\(^2\)) embedded in the conduction band of the solid, that can decay by electron emission [22]; this state would release upon decay the same energy as a free \(F^{-}\), leading to the production of electrons of a few eV. Electron energy loss (EELS) measurements and theoretical studies of LiF and MgO do not show evidence of such doubly-excited states in the solid; one can furthermore expect that the excitation energy of this putative state in the solid should be very different from that of a free ion. A simpler explanation is that the decay of the excitons into vacuum (or exciton break-up [23]) produces electrons with an energy distribution peaked at the observed low energies, due to the small (positive) difference in energy between the exciton and the vacuum level.

In conclusion, the energy distribution of electrons emitted from MgO surfaces under the impact of slow singly charged noble gas and sodium ions shows a remarkable independence of the type of incident ion and energy. This result shows that electron emission results from the decay of an intrinsic excitation in the solid. We propose that excitons produced by electron promotion during binary projectile-oxygen collisions decay into vacuum due to the negative electron affinity of the surface.

References


