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Role of the resistivity of insulating field emitters on the energy of field-ionised and field-evaporated atoms

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ABSTRACT

In order to improve the accuracy of laser atom probe analyses, it is important to understand all the physical processes induced by the combination of the high electrical field and the femtosecond laser beam during field evaporation.

New information can be accessed from the energy of evaporated surface atoms or field-ionised atoms of an imaging gas. In order to study the ions energy, we combine La-APT and FIM analyses in a new experimental setup equipped with electrostatic lenses.

We report measurements for semiconductors and oxides and we study the influence of the illumination conditions (laser power and wavelength), the evaporation rate, the sample geometry and the tip preparation processes. The results are discussed taking into account the resistive properties of non-metallic samples and the photo-stimulated conductivity.

This work clarifies the role of the laser and DC field in the energy deficit of field evaporated ions.

1. Introduction

Thanks to the use of fast-laser pulses, Laser assisted atom probe tomography (La-APT); 3D nanoanalysis is now possible for a wide range of materials. In addition to metals, it is now possible to analyse not only semiconductors but also ceramics and oxides [1–7]. The quantitative analysis of this class of materials is challenging in many aspects. For instance, the ability to quantitatively measure composition reliably is particularly attractive when dealing with oxides that are able to accommodate high concentrations of point defects [8]. The analysis of highly resistive materials is also of fundamental importance in the field of microelectronics, including the challenging aspect of finding and analysing local interfaces between the structures of a functional device [9]. In the early years of APT, only nanometres scale oxide inclusions in metals or highly conductive oxides were studied [10–13]. The first published work on the atom probe analysis of bulk insulator was performed by Kellogg in the early eighties [14]. The analysis was found tedious and a thin metal coating was used to improve the electrical conduction. This requirement was thought essential to avoid the huge voltage drop that should be observed between the end apex of the sample and the base where the high voltage is applied. Thereafter, progresses in the analysis of oxides were slow, and the electrical resistivity was thought to be one of the main limitations of the technique. Only recently, with the large spreading of modern laser assisted APT instruments all over the world, a blooming of studies in APT of oxides and ceramics was observed. Surprisingly, successful analyses of uncoated specimen were obtained for several bulk ceramics [15–16]. In addition near atomic scale resolution was demonstrated.

These observations question our understanding of field evaporation for the case of poorly conductive materials. In a simple approach, in atom probe, the field emitter must drain the charge induced by pulsed field evaporation. The analysed bulk dielectric material is generally a micron size sample attached to a macroscopic metallic needle. It may then be considered as an electrical resistor which resistance can be considered to be very high especially at the cryogenic temperatures used (10^{10}–10^{20} Ω). Kellogg predicted several kV of voltage drop for fused glass or Pyrex samples. Nevertheless, in recent experiments, voltage drops are rarely observed. Only in the paper of Chen et al. [17], a drop of only a few volts was measured in MgO samples. Chen et al. and after Tamura et al. [18] proposed a model based on accumulation of photo-induced holes changing the internal and external electric field around the tip apex. This paper shows the important role of the laser excitation in the field evaporation process. Some other authors pointed out the importance of surface states in the actual electrical properties of the sample. For instance, ab-initio calculations suggest that the band gap of crystalline alumina is reduced from ~8 eV in the bulk to 2.5 eV at the surface, which makes the alumina surface more conductive and more absorbing in the visible domain of the laser excitation used (532 nm laser pulse/

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2.3 eV or 355 nm/3.6 eV). The presence of Ga and the possible amorphization of the oxide surface by the gallium beam during sample preparation in the focused ion beam instrument may also contribute to a modification of the surface states and thus may create a charge-draining path, much like coating with a thin metal layer. The presence of the surface field may also change the physical properties of the material, as calculated by Kreuzer et al. [19]. In addition, the high surface to volume ratio of an APT sample may enhance the effects of any modification of the surfaces electrical properties.

In this work, several experimental procedures were developed to accurately measure the in-situ electrical resistance of the APT sample. In order to measure the voltage drop with a high accuracy, electrostatic lenses are introduced in the chamber. The setup is then used as an ion energy analyser, which amplifies the effect of the ions energy on their trajectories and time of flight. This enables an accurate measurement of the voltage drop using the relationship: $\Delta E = ne\Delta V$, with ne the ion charge. With such an experimental setup we are able to investigate voltage variations at the tip apex ranging from a few volts to hundreds of volts.

To amplify the observed voltage drop, the FIM mode was used in addition to the APT mode. The ion current can, indeed, be increased by several orders of magnitude due to the contribution of the ionisation of the image gas. The variation of the observed resistance of semiconductors and oxide tip samples were studied. We demonstrate that the laser illumination creates free carriers in the material, which significantly reduce its resistivity. After the laser pulse, these carriers recombine up to an average equilibrium value. In the case of FIM measurements, this average carrier density is monitored. The role of the specimen preparation is also addressed.

2. Theoretical consideration

The ion energy deficit is induced by the voltage drop ΔV existing between the tip apex and its metallic base. Two different effects contribute to this voltage drop: the Ohmic effect and the Band Bending Effect [20]. Indeed, the expression of the drop can be written:

$$\Delta V = V_0 - V_{tip} = \Delta V_{bb} + \Delta V_{Ohm} = \Delta V_{bb} + RI \quad (1)$$

where ΔV_{bb} is the voltage drop induced by the change of band gap created by the accumulation of holes, I is the electronic current inside the tip (equal to the ionic current emitted from the tip) and R is the resistance of the tip. This resistance is given in a first approach by

$$R = L_{tip}(\mu_c n_c e S_{tip})^{-1} \quad (2)$$

where $S_{tip} = \pi r_{apex} r_{base}$ [21] is the mean tip cross section, μ_c the carrier mobility and n_c the carrier density [22]. In the case of semiconductors analysed by La-APT, both the ionic current and the resistance are low: the resistive effect is negligible and the voltage drop at the tip apex is smaller than 1 V. In FIM mode, the ionic current is higher than in La-APT mode (more than a factor 1000) so the contribution of this resistive effect can be observed even during the FIM analysis of semiconductors. In the case of oxides like MgO, the resistance is so high that the ohmic contribution can become the main contribution to the voltage drop.

3. Experimental setup and methods

Two types of materials were analysed: silicon (Si) and MgO.

Si tips were prepared by annular milling from micro-post [24] of around 3 μm in radius and 40 μm in length. Two types of micro-posts were analysed: un-doped $<100>$ oriented micro-posts and p-doped (10^{18} cm^{-3}) $<111>$ oriented micro-posts.

MgO tips were prepared from bulk samples using the lift-out method [25,26].

All measurements were performed on a FlexTAP instrument (CAMECA) in APT mode or FIM mode. The main characteristic of the FlexTAP is the presence of three electrostatic lenses, between the tip and the detector, which can be polarised to accelerate of decelerate the emitted ions. This setup was developed in order to offer a flexible angle of view on the tip during the analysis: ranging from 4° to 30°. The other main goal is to improve the temporal resolution of the ToF spectrum. The relative accuracy of ToF measurements depends on the ratio of the ion ToF (t) over the time accuracy of the detector (Δt). The lenses allow to increase the value of ToF (t) and hence the accuracy of its measurement. The FlexTAP is coupled to a femto-second pulsed laser, with a repetition rate of 50 kHz in APT mode and 100 kHz in FIM mode, a pulse duration of 500 fs and a tuneable wavelength (1030 nm, 515 nm and 343 nm).

The FIM is a projection microscope, which images the tip surface with an atomic resolution [23]. Noble gas atoms are introduced in the analysis chamber and are field-ionised close to protruding surface atoms, where the field is highest. After the ionisation, these ions are projected onto a grounded screen. The ionisation of the gas atoms by tunnelling effect requires a high electric field, around tens of volts per nanometre, which is of the same order than the field for field-evaporation in APT mode. Neon gas was used as imaging gas in the following experiments.

The main advantages of FIM for the following experiments are that:

1. The ionic emission current I (and the electronic current inside the tip) is between 1000 and 10,000 times higher than in the case of APT.
2. FIM images can also be obtained without laser illumination, hence the voltage drops with and without laser illumination can be compared. This is not the case for APT analysis, where the laser power can be varied, but cannot be zero as laser pulses are required for TOF measurements.
3. Because the tip surface is not evaporated, the sample geometry remains constant during the experiment.

The FIM detector is placed at 44.5 cm from the tip. An aperture is placed in front of the tip, and stops ions emitted at too large angles, that can have aberrant trajectories. The ion trajectories are schematically represented in Fig. 1 for fields of view of 30° and 15°. The voltages applied to the lenses for these two modes are given in Table 1.

The 15° mode was used in the case of small voltage drops at the tip apex. Indeed, only one lens is polarized, hence, the relationship between the voltage drop and the shift of trajectories is easier to predict. Moreover, the magnification of this mode is larger than of the 30° mode, which causes the ions trajectories and TOFs to be more sensitive to small variations in V_{tip}. The main problem of this mode, however, is the high value of the potential applied to the decelerating lens: it is higher in the case of the 30° mode (1.005 against 0.982), inducing a high potential barrier on the ions trajectories. Therefore, if the energy deficit is important (higher than about 1.5%), the ions can be repelled and not reach the detector.

The 30° mode, to the contrary, was chosen to measure energy deficits as high as a few percent. One advantage of this mode is its large field of view, which enables to collect more spatial information because the area imaged on the tip surface is 4 times larger. However, one drawback is that when the ions have high energy deficit, their trajectories can exhibit strong aberrations, as discussed later.

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