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Atom probe tomography of lithium-doped network glasses

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ARTICLE INFO

Article history:

Received 2 February 2014

Received in revised form

14 March 2014

Accepted 16 March 2014

Available online 21 March 2014

Keywords:

Atom probe tomography
Laser-assisted field evaporation
Dielectric materials
Band bending
Ionic transport

ABSTRACT

Li-doped silicate and borate glasses are electronically insulating, but provide considerable ionic conductivity. Under measurement conditions of laser-assisted atom probe tomography, mobile Li ions are redistributed in response to high electric fields. In consequence, the direct interpretation of measured composition profiles is prevented. It is demonstrated that composition profiles are nevertheless well understood by a complex model taking into account the electronic structure of dielectric materials, ionic mobility and field screening. Quantitative data on band bending and field penetration during measurement are derived which are important in understanding laser-assisted atom probe tomography of dielectric materials.

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1. Introduction

Atom probe tomography (APT) is an outstanding tool of 3D chemical analysis in atomic resolution [1,2]. Tip-shaped samples of curvature radii below 100 nm are subjected to high electric fields to evaporate individual ions which are detected by a 2D detector and identified by time of flight spectroscopy. From a set of few millions of detected events, a 3D map of the original atomic arrangement is reconstructed. In conventional atom probes, evaporation is triggered by high voltage pulses. This restricts the method to conductive materials. A recent extension by laser-assisted evaporation modes opened the method to measurement of dielectric materials [3–6].

This success raised new questions concerning the evaporation mechanism and laser–tip interaction. A consensus seems to be reached that pulsed local heating represents the dominant trigger mechanism in laser-assisted evaporation [7–9]. For this, a significant amount of laser energy has to be absorbed by the specimen. Remarkably, however, even materials with a band gap well above the photon energy are efficiently evaporated, even though they are fully transparent to the laser light. For the case of semi-conductors, it has been suggested that pronounced band bending at the tip surface [10,11] plays an important role in the laser–tip interaction. It is unclear as to which extent this concept can be applied to dielectric materials with significantly larger band gaps. A recent study by Silaeva et al. [12] indicated a generation of free charge

carriers and the reduction of band gap for different oxides and semiconductors under high fields and laser irradiation. Thus simpler models based on sole thermal interaction between the laser and the specimen may have a limited validity (see a recent review on the topic in Ref. [9]).

In addition, dielectric materials bear particular difficulties in tomographic reconstruction. Numerical simulations predict that dielectrics at the tip apex can induce significant field distortion if the electric field deeply penetrates the dielectric precipitates at the surface, with the immediate consequence of severe reconstruction artifacts [13]. To estimate such effects, a realistic measurement of band bending and field penetration under the high-field conditions of laser-assisted APT (LA-APT) would be important. Here we demonstrate that analyzing ion conductive glasses provides a tool to estimate field penetration quantitatively.

2. Materials and methods

In our study, we analyzed thin films of different Li-doped borate or silicate glasses (e.g. 0.35 Li₂O - 0.65 SiO₂, 0.15 Li₂O - 0.85 B₂O₃) by LA-APT. Borate or silicate units form a rigid, amorphous network. By doping with Li₂O, immobile anionic defects (non-bridging oxygen, tetrahedral BO₄⁻ groups) and mobile Li⁺ cations are introduced into this network [14–16].

Thin layers of both glasses, about 10 nm in thickness, were deposited on pre-shaped tungsten tips (field developed up to 14 kV) by ion beam sputter deposition. A part of them was additionally coated by conductive Al to shield the glass layer first from the field when starting the measurement. APT analysis was

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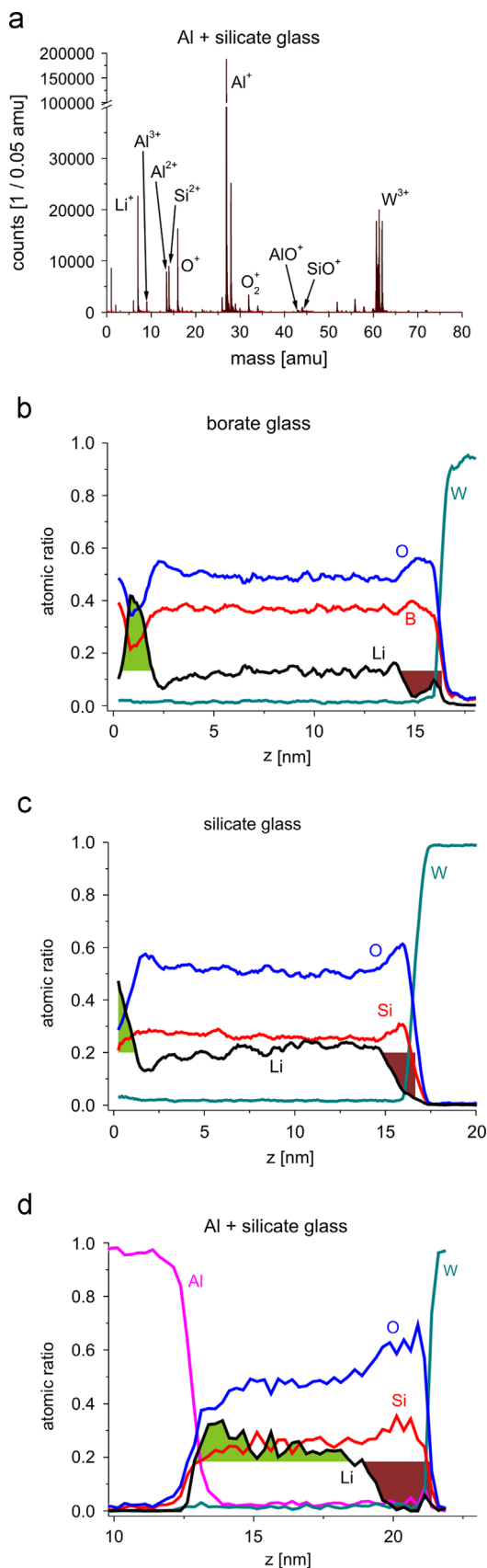


Fig. 1. Atom probe analysis of layered glass samples: (a) Mass spectrum of Li silicate glass coated by an Al capping layer. (b–d) Composition profiles traced perpendicular to layer interfaces, different glasses and layer stacks as indicated. Li enrichment at the surface; the front-side interface toward Al is highlighted in green, depletion at the back-side interface to W substrate in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

carried out using the laser-assisted atom probe in Münster [6] using a laser wavelength of 345 nm, a pulse energy and length of 75 nJ and 250 fs, respectively, at a 200 kHz repetition rate. Tips were cooled to a base temperature of 100 K.

3. Results and discussion

Though mass spectra are quite complex, all peaks are unambiguously identified (see the example of 0.35 Li₂O - 0.65 SiO₂ in Fig. 1(a)). From 3D reconstruction, we derive one-dimensional composition profiles along the tip axis (see examples in Fig. 1(b–d)). In all the studied examples, we do observe an unexpected but pronounced enrichment of Li at the surface (partial figures (b) and (c)) or at the interface between Al and the glass layer (Fig. 1(d)) and in correlation a clear zone of depletion at the back-side toward the tungsten substrate.

Regarding details of the observed composition profiles, this effect of Li redistribution cannot be explained by mere preferential evaporation of Li; for example it is noticed that the concentration rise of Si and O at the transition from Al to the glass layer is even slightly ahead of the Li rise (Fig. 1(d)) which strongly indicates that spatial redistribution of Li needs some time. This points to the electromigration of Li ions. Obviously Li ions are shifted continuously toward the surface during the measurement. As will be shown, a diffusion coefficient in the range of 10^{-21} to 10^{-18} m² s⁻¹ is required to allow such redistribution. At the nominal temperature (100 K), Li diffusivity of the studied silica glass would be only about 10^{-43} m² s⁻¹. However, a temperature rise during the laser pulse by about 200 K would be sufficient to reach the required mobility. Such a temperature rise is realistic based on reported results [17].

Below we present a model to understand the observed features of the composition profiles. Let us assume that a 1D description perpendicular to the tip surface is sufficient. The electric field applied to the tip partly penetrates the dielectric glass layers (at least as soon as the shielding Al layer has completely evaporated). Then, redistribution of the Li ions develops according to

$$j_{\text{Li}}(x) = -D_{\text{Li}} \frac{dc_{\text{Li}}(x)}{dx} - E(x)eD_{\text{Li}} \frac{c_{\text{Li}}(x)}{kT}, \quad (1)$$

with D_{Li} , $c_{\text{Li}}(x)$, and $E(x)$ being the diffusion coefficient, local concentration of Li, and local field, respectively. Physical constants e and k and variable T have their usual meanings. As mentioned before, diffusion of Li can only take place during the laser pulses, i. e. only a fraction of the total measurement time.

If the glass behaved purely dielectrically, Maxwell's equations would predict a constant field $E_{\text{ext}}/\epsilon_r$ across the glass layer so that the band edges become sloped as presented in Fig. 2a for realistic parameters (band gap of 7 eV; external field 30 V/nm; $\epsilon_r=5$; and layer thickness 7.5 nm). However, Tsong already pointed out the impact of high electric fields on the band structure of semiconductors and calculated the consequent band bending [10]. It is controversial whether the required electronic defects could also be generated in strong insulators. But here, due to a strong slope of the band edges, the spatial separation between the valence and conduction band would decrease to the order of 1 nm and thus mobile charge carriers could even be produced by tunneling if no alternative mechanism of carrier generation [12] was activated (Fig. 2a). Therefore, our model assumes that occupation of electronic states adapts immediately to the local potential (Fig. 2b). Afterward, we will check this assumption by a comparison of model predictions with the LA-APT experimental data. For the sake of simplicity, we will consider here a model in which the Fermi-level of the material remains constant during the APT measurement.

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