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Understanding of the field evaporation of surface modified oxide materials through transmission electron microscopy and atom probe tomography

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ABSTRACT

Understanding of triggering the field evaporation of surface ions on the non-conductive materials enables improvement in the mass resolution in laser-pulsed atom probe tomography. This study addresses the influence of surface modification through metallic-capped layers, such as Co, Ni, and Ag, with surrounding bulk MgO tips on the physical mechanisms responsible for field evaporation and on the mass resolving power compared to uncapped bulk MgO. In particular, the field evaporation on the surface regions of Ag-capped bulk MgO tips during analysis was extensively observed by transmission electron microscopy to confirm the overall evaporation sequences occurring at the tip surface. We found that the introduction of such capping layers, especially for Ag-capping, controls both symmetric tip geometry at the surface of the specimens and the mass resolving power of ion species consisting of MgO materials. This implies the improvements in the symmetries of local field distributions and the isotropy of thermal heating across the tip surface. It reveals that Ag-capping with high thermal diffusivity promotes the compositional uniformities between the laser illumination side and the opposite side for MgO samples as well as the reduced fraction of multiple events for oxygen ions between both sides. Moreover, a variation in the thickness of the Ag-capping layer is an additional factor governing a thermal-assisted mechanism of MgO evaporation. Based on our findings, homogeneous thermal heat transfer for MgO emission along the tip axis by Ag-capping layers may be significant in potential methods for improvement.

1. Introduction

Atom probe tomography (APT) is a time-of-flight mass spectrometry-based microanalysis technique that involves triggering the field evaporation of surface atoms of a tip-shaped specimen under an extremely high surface electric field [1,2]. The field-evaporated ions are identified by employing their times of flight (TOF), called TOF mass-spectroscopy, and are hence reconstructed by three-dimensional (3D) atomic mappings. The method enables 3D characterization for deeper understanding of the chemical nature of conductive materials at the nanometre/atomic level because of its high depth, spatial resolutions, and ppm-level sensitivity [3–5]. Indeed, the technique has been commonly used to investigate the elemental partitioning in the multiple phases [6–10]; the segregation of solutes to the boundaries [11], interfaces [12], and dislocations [13] the cluster formation [14–16], and the equilibrium precipitates [17,18]. After the introduction of laser-pulsed APT, this microscopy can be performed in nonconductive materials such as heterogeneous structures consisting of metals and NiO thin-films; thus, bulk oxides have recently been successfully analyzed [19–24].

Two interpretations of the underlying mechanisms explaining the field evaporation of surface atoms in nonconductive or insulating materials during laser pulsed APT have been reviewed by Vella [24], i.e., photo-ionization process and thermal-induced evaporation. The evaporation behavior of the doped oxides was mainly controlled by the former process associated with optical material properties [25,26]. On the other hand, the latter process without the photo-ionization process becomes the main mechanism responsible for bulk un-doped oxides with high band-gap energy [27]. Following this concept, inhomogeneous apex heating on the surface of APT tips is commonly found at the surface region during

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laser-induced thermal evaporation [28–31]. Thus, the strong interaction between laser pulses irradiated to the tip surface and oxide materials is highly complex [32–34]. This complexity leads to the ongoing debates concerning experimental conditions, especially laser pulse energy. For instance, there is severely asymmetric evaporation between the laser-exposed side and the side farthest from the laser incidence (termed the shadow side) under a relatively high laser fluence. This so-called "shadow effect" is due to the confined absorption of laser light [29,30], resulting in the reduction of the mass resolving power for APT of oxide materials. Because the ions originating from the shadow side, which is far from the incident laser direction, require a longer cooling time than those in the laser side, long thermal tails in the mass resolution are inevitable. Among the various oxide materials, bulk MgO is the most extensively used material in spintronics and microelectronics as an insulator with wide band gap energy, owing to its conductivity of 45 W/(m K) and band gap of 7.8 eV. Thus, gaining better mass resolving power in the mass spectra obtained from bulk MgO materials as well as the enhanced TOF becomes an essential topic when triggering the field emission of MgO by laser-pulsed APT.

A recent effort proposed by Larson et al. [35] was made to achieve the enhanced mass resolving power of SiN by means of depositing the Pd/Ag metallic capping onto the AP tips. This approach enables more uniform heat flow from Pd/Ag layers to the substrate SiN layer with increasing thermal diffusivity of the SiN tips under laser-pulsing. Note that the concept of "coating" and "capping" is different; i.e., the former indicates that the protection layers such as Al, Ni, or Si metals are deposited onto the surface of the materials prior to preparing the needle-like tips, whilst the latter means that after preparing the AP needles, the metals with high thermal diffusivity are capped or deposited onto the surface regions surrounding the tip. To date, however, there is a lack of experimental data to explain the underlying physical mechanism of such capping effects on the elemental evaporation of bulk oxides. In addition, very few studies have been undertaken to reveal the mechanism responsible for the field evaporation in metal-capped bulk MgO oxide with/without doping, except for un-capped oxides [24–27]. Therefore, a specific challenge for advanced APT analysis lies in revealing the effects of metallic capping layers on the mass resolving power of APT measurements for MgO materials. Here, the Co, Ni, and Ag layers were deposited onto MgO tips as the metallic capping layers as shown in Fig. 1. And thus, additional efforts were made to modify the geometrical parameters such as shank angle and tip radius of MgO needles, which govern the field evaporation strength, the mass spectra, and the reconstruction algorithm of the APT data set.

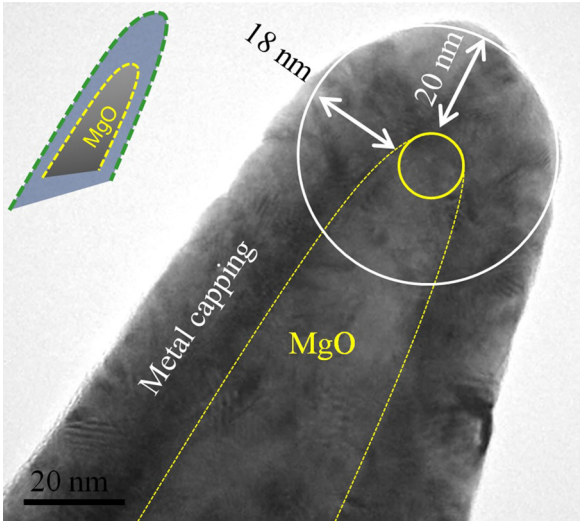

Fig. 1. TEM image of metallic-capped MgO tip proposed in this study and the corresponding schematic illustration. All capping layers deposited on the MgO tips have thicknesses of 20 nm on the top surface, and 18 nm for the side surrounding the apex surface.

More specifically, it is the aim of this study to deeply understand the underlying mechanism of the field evaporation of bulk MgO materials. To regulate this issue, we observed the changes of the mass spectra taken from MgO oxides with respect to the application of metallic capping layers varying with their thicknesses, paying particular attention to tip morphological evolution before, during, and after APT experiments in conjunction with transmission electron microscopy (TEM). Indeed, our approach of a step-wise APT with TEM observation could provide a hint regarding the APT data reconstruction methodology [36,37], outlining the overall evaporation sequences at the tip surface [38]. We expect that an atomic-scale insight into the fundamental study of bulk MgO materials can provide large interest in the fields of spintronics and microelectronics. Moreover, this work can provide potential breakthroughs for improving the performance and applicability of APT experiments for oxide materials in terms of metal capping.

2. Experiments

Un-doped bulk MgO single-crystals with a growth direction of [001] were used in this context. The needles for APT were prepared using a dual-beam focused ion beam (FIB, Helios Nano-Lab 600*i*) lift-out method [39,40]. Finally, low-energy milling at an acceleration voltage of 1 kV was used to minimize Ga-ion damage. Next, various metallic capping materials were deposited onto the FIB-prepared needles of MgO through radio frequency (RF) plasma sputtering for 3 min at a temperature of 300 K. In this work, three capping materials of Ni, Co, and Ag were used. The sputtering conditions governing the thickness of metallic capping layers were controlled with specific care, because of their different sputtering yields and deposition rates. In particular, the thickness of the top surface along the tip apex and side surrounding the apex surface for all capping layers was estimated to be 20 and 18 nm, respectively (called thermal diffusivity effects). Here, efforts were made to precisely control the gas pressure. And then, the thickness of Ag layers deposited onto the FIB needles was controlled in the range of 20–100 nm to classify the thickness effect (called geometrical effects).

The APT analysis was performed using a laser-assisted wide-angle tomographic AP (LAWATAP, CAMECA^{TM}) operating in a UV laser mode under ultra-high vacuum with a pulse repetition rate of 100 kHz. Laser pulse energy of up to 20 μJ was applied, corresponding to effective pulse fractions of 10–40%, as determined by the calibration method proposed previously [41]. The total voltage during probing was in the range of 3–6 kV. The evaporation rate was fixed in the range of 0.001–0.005 atom/pulse. Measurements containing ~2.0 million atoms at each data set were collected at a tip temperature of 40 K. The raw data were reconstructed with both TAP3DDATA software and IVAS software using shank angles and tip radii measured by a JEM 2100F microscope operated at 200 kV. In this paper, the Mg^{2+} peaks are assigned to 11.99, 12.49, and 12.99 Da, and 39.98, 40.98, 41.98 Da are assigned for MgO^{+}. In particular, the Mg_2O^{2+} and O_2^{+} peaks detected at 32 and 33 Da were decomposed via the TAP3DDATA and IVAS software algorithms. According to the natural abundance of oxygen isotopes $32O^{2+}$, $33O^{2+}$, and $34O^{2+}$, the contribution of $32O^{2+}$ to peak 32 Da and $33O^{2+}$ to peak 33 Da can be estimated by its relative abundance ratio to $64Mg_2O^{2+}$ and $66Mg_2O^{2+}$, respectively.

To observe the morphological evolution in the surface regions of the tip apex containing metallic capping layers and to ensure the evaporation sequence at the tip surface occurring during APT, the