

## Investigation of an oxide layer by femtosecond-laser-assisted atom probe tomography

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In this letter, we report results obtained from the atom-probe tomography (APT) analysis of an oxide layer developed on a pure iron specimen under low pressure of oxygen. These specimens are generally fragile, and hard to analyze in APT. Here we show that by the use of femtosecond laser pulses, the oxide layer could be field evaporated atom by atom allowing its chemical identification at the atomic scale. The evidence of iron atomic planes through the whole oxide layer suggests that oxygen atoms diffuse through the oxide layer during the first stages of the oxidation process. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186394]

Oxide layers a few nanometers thick are involved in a wide domain of applications: giant magnetoresistance, tunnel barrier based devices, or more simply in coatings for surface treatment. As a result, the chemical analysis of such layers requires an investigation on a nearly atomic scale. Among the analytical techniques used in materials sciences, the atom-probe tomography (APT) is the only one capable of mapping out the chemistry of a material at the atomic scale and in three dimensions in a volume of the order of  $10^5 \text{ nm}^3$ .<sup>1,2</sup> In the APT, single atoms are removed from the surface of a tip-like-shaped specimen surface by field evaporation. The tip is cooled down to cryogenic temperatures (20–80 K) to avoid surface atom migration under the effect of the electric field. To obtain the intense electric field (a few  $10^8 \text{ V nm}^{-1}$ ) the tip is biased at high voltage (10 kV). In order to accurately know the moment at which atoms are ionized and removed from the surface, a fraction (typically 20%) of this voltage is applied by means of high voltage pulses (rise time 1 ns). These ions are then radially projected onto a position-sensitive detector where they are chemically identified by time of flight mass spectrometry (TOF-MS) and positioned. Because of the small tip radius of curvature (50 nm), the magnification is very high, reaching  $10^6$  for a tip to detector distance of 0.5 m. Knowing this magnification, the probed volume can be reconstructed in three dimensions layer after layer. This unique in-depth atomic resolution is achieved because the electric field penetration depth is below 0.01 nm at the tip surface for conductive materials.

The capabilities of the conventional APT in material sciences has already been demonstrated in the past.<sup>2–4</sup> However, because high voltage (HV) pulses are required, samples have to be good conductive materials. In poorly conductive materials, fast HV pulses cannot be efficiently transmitted to the tip apex.<sup>5</sup> Due to the whole electrical environment (chamber walls), the instrument behaves as a low pass filter with a cutoff frequency proportional to the conductivity of the material. As a result, long pulses (100 ns) are required to field evaporate atoms from a specimen with a resistivity over

$10^2\text{--}10^3 \text{ } \Omega \text{ cm}$  at room temperature, making it impossible an accurate chemical identification by TOF-MS.<sup>6</sup> Another consequence of the resistivity is an inhomogeneity of the electric field at the tip surface, leading to the evaporation of clusters of a few atoms. In the case of oxidized materials analysis, the oxide layer is often observed to be removed at once as soon as HV pulses are applied, leading to the premature rupture of the specimen.<sup>2</sup> Even when the analysis is possible, the instrument is taken to its intrinsic limitation by the evaporation behavior of the sample and this prevents the system to work properly on this kind of materials. Recently we have shown that the field evaporation can be assisted by ultrashort laser pulses (typically 100 fs)<sup>7,8</sup> superimposed to the standing voltage. In the laser-assisted-APT (LA-APT), because of the subwavelength dimensions of the tip, the laser field is enhanced at the tip apex leading to values matching that required for field evaporation. This enhancement appears on metals but also on poorly conductive material tips.<sup>9,10</sup> The LA-APT analysis of poorly conducting or even nonconducting materials should thus be possible in the LA-APT.

To study the very first steps of oxidation of a pure iron surface under oxygen atmosphere, an oxide layer was formed by annealing for 15 min at 773 K pure iron tips under low pressure of  $\text{O}_2$  ( $10^{-6}$  mbar). Specimens were investigated both by conventional APT and by LA-APT. The LA-APT was equipped with a amplified femtosecond laser based on ytterbium doped crystals (pulses duration:  $\approx 350$  fs, energy per pulse:  $100 \mu\text{J}$ , wavelength: 1033 nm, repetition rate: 2000 Hz). The focusing on the tip apex was made through a glass window in the ultrahigh-vacuum chamber with a lens (focal length 25 cm). The wave polarization was set along the tip axis by means of a half-wave plate. TOF-MS and positioning of ions was made with a fast charge-coupled device-based time-resolved position-sensitive detector.<sup>11</sup> Results from the LA-APT analysis of the oxidized iron tip are strikingly different from those obtained by conventional APT. First, the oxide seems to be removed atom per atom in contrast to the conventional APT where the evaporation occurs mainly cluster by cluster. This is clear in Fig. 1 giving the distribution of efficient pulses leading to the detection of single and multiple events as obtained from LA and HV APT

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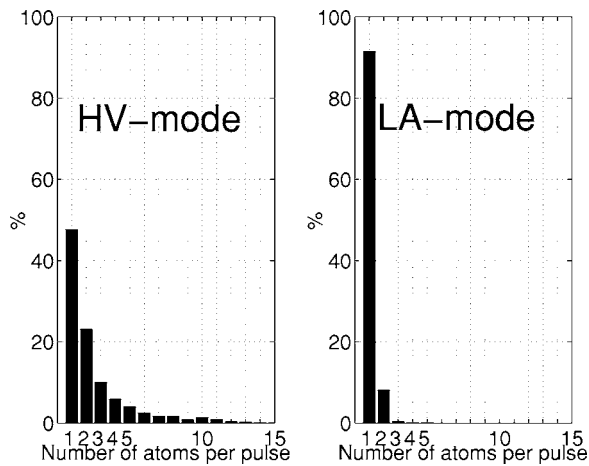


FIG. 1. Distribution of the number of atoms evaporated on efficient pulses in HV mode (left) and LA mode (right).

analyses performed at comparable detection rates. Under HV pulsing, the proportion of multiple events is above 50% as commonly observed on poorly conductive materials while it represents less than 20% under laser pulsing. A first explanation for this difference is the much shorter duration of laser pulses that is below the atom vibration time (a few ps) in contrast to HV pulses. This results in a correspondingly lower probability of field evaporation and consequently of multiple evaporation. The large number of multiple events observed under HV pulsing can also be explained by the much higher probability of postdissociation of evaporated molecules or clusters next to the tip surface. The pulsed voltage is still present when evaporated molecules cross the dissociation zone where the electric field is sufficient to make an electron tunnel from the evaporated ion or molecule to the tip.<sup>12</sup> This is in agreement with the differences between the observed Fe charge states reported in Fig. 2. Fe is mainly 2+ charged under HV pulsing while 1+ and 2+ charge states are observed under laser pulsing. Due to the very short duration of laser pulses, the pulsed electric field is off when the ions pass through the postionization zone.

Surprisingly, as shown in the three-dimensional (3D) image [Fig. 3(a)] the oxide layer is not homogeneous but made

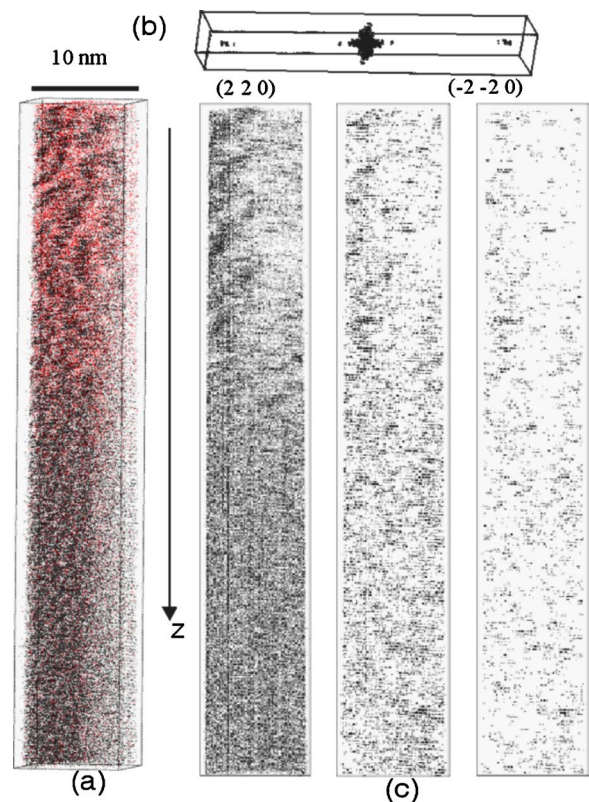


FIG. 3. (a) 3D image of the oxidized iron (in black: Fe, in red: molecular FeO). (b) Diffraction pattern obtained by Fourier transform. The spots correspond to (220) planes. (c) Filtered 3D images of the Fe atoms by inverse FT on the (220) diffraction spots. The filter threshold is progressively increased from left to right to refine the atomic planes structure.

of a pure iron rich region mixed with an oxidized iron region. By applying Fourier transform procedures on the 3D data set, one can obtain dark or bright field images of the analyzed volume.<sup>13</sup> By selecting the diffraction spots [Fig. 3(b)] related to (220) Fe planes a filtered image of the atoms located in these planes can be reconstructed [Fig. 3(c)]. Note that the atomic planes are revealed both in the pure iron substrate and in the Fe rich region within the oxide layer. The continuity in the order strongly suggests that oxygen diffused

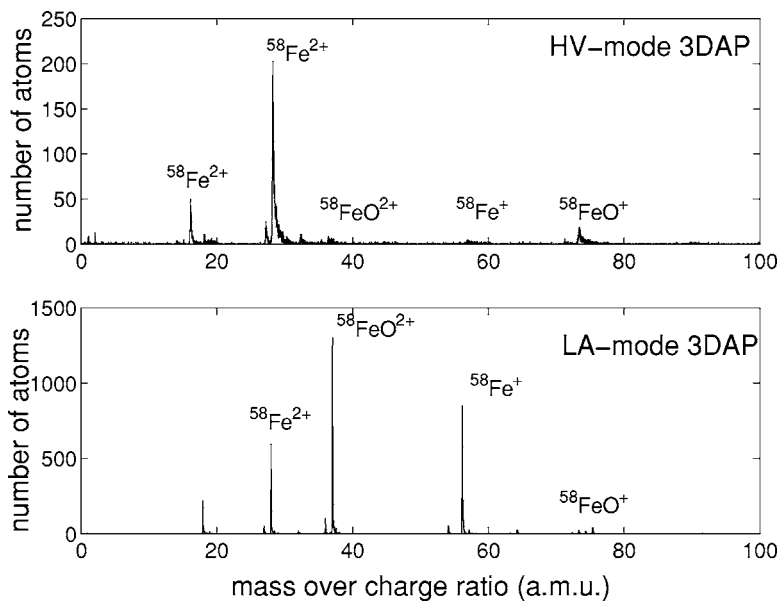


FIG. 2. Mass spectra related to the analysis of the oxide in HV-APT (top) and LA-APT (bottom). Please note the mass resolution improvement by the use of laser pulses.

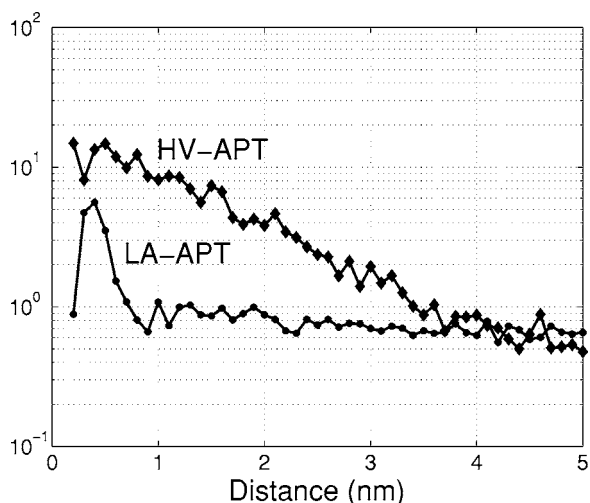


FIG. 4. Distributions of distances between atoms evaporated on a same pulse under HV pulsing and laser pulsing.

into the iron substrate during the oxide formation.

The ability to resolve atomic layers demonstrates the accuracy of the reconstruction of the analyzed volume. No evidence of atomic planes could be observed in the image obtained with the HV-APT. This tends to indicate strong differences in the way the field evaporation occurs under laser illumination and under HV pulsing. The APT ability to reveal the order in a material strongly depends on the so-called co-evaporation process. When a kink site atom is removed, neighboring atoms are suddenly submitted to a higher EF so that they are likely to be evaporated on the same pulse. Figure 4 shows what we call a correlation function of distances between two ions removed on a same pulse as obtained from LA-APT and HV-APT analyses. The correlation function is the ratio between the experimental distribution and a theoretical random distribution. In the case of the LA-APT, the correlation function shows a sharp peak located at around 0.4 nm, close to the Fe lattice parameter,

that rapidly decreases down to a plateau corresponding to the random value that should be observed if atoms were evaporated independently from each other. In the case of the HV-APT, the distribution is much broader indicating the presence of significant correlation in the way atoms are removed. These results suggest a better homogeneity of the pulsed electric field on the whole specimen surface under laser illumination. They also tend to demonstrate that the enhanced laser field responsible for the atom removal is confined at the surface of the material and is screened in the very first atomic layers in the material. The use of ultrafast laser pulses seems a promising way for extending the field of application of APT to the investigation at the atomic scale of poor conductive materials.

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<sup>1</sup>D. Blavette, B. Deconihout, A. Bostel, J. M. Sarrau, M. Bouet, and A. Menand, *Rev. Sci. Instrum.* **64**, 2911 (1993).

<sup>2</sup>M. Müller, A. Cerezo, M. Hetherington, and G. Smith, *Atom Probe Field Ion Microscopy* (Oxford Science, Clarendon, 1996).

<sup>3</sup>D. Blavette, A. Bostel, J. Sarrau, B. Deconihout, and A. Menand, *Nature (London)* **363**, 432 (1993).

<sup>4</sup>D. Blavette, E. Cadel, A. Fraczkiewicz, and A. Menand, *Science* **286**, 5448 (1999).

<sup>5</sup>G. Kellogg and T. Tsong, *J. Appl. Phys.* **51**, 1184 (1980).

<sup>6</sup>A. J. Melmed, M. Martinka, S. M. Girvin, T. Sakurai, and Y. Kuk, *Appl. Phys. Lett.* **39**, 416 (1981).

<sup>7</sup>B. Deconihout, F. Vurpillot, B. Gault, G. da Costa, M. Bouet, A. Bostel, A. Hideur, G. Martel, M. Brunel, and D. Blavette, *Surf. Interface Anal.* (accepted).

<sup>8</sup>B. Gault, F. Vurpillot, A. Bostel, A. Menand, and B. Deconihout, *Appl. Phys. Lett.* **86**, 094101 (2005).

<sup>9</sup>G. T. Boyd, T. Rasing, J. R. R. Leite, and Y. R. Shen, *Phys. Rev. B* **30**, 519 (1984).

<sup>10</sup>L. Novotny, R. X. Bian, and X. S. Xie, *Phys. Rev. Lett.* **79**, 645 (1997).

<sup>11</sup>B. Deconihout, L. Renaud, G. Da Costa, M. Bouet, A. Bostel, and D. Blavette, *Ultramicroscopy* **73**, 253 (1998).

<sup>12</sup>R. Haydock and D. R. Kingham, *Phys. Rev. Lett.* **44**, 1520 (1980).

<sup>13</sup>F. Vurpillot, G. Da Costa, A. Menand, and D. Blavette, *J. Microsc.* **203**, 295 (2001).