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Laser pulsing of field evaporation in atom probe tomography ☆

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ABSTRACT

The processes by which field evaporation in an atom probe is momentarily stimulated by impingement of a laser beam on a specimen are considered. For metals, the dominant and perhaps only sensible mechanism is energy absorption leading to thermal pulsing, which has been well established. The energy of a laser beam is absorbed in a thin optical skin depth on the surface of the specimen. For materials with a band gap such as semiconductors and dielectrics, it is found that energy absorption in a thin surface layer dominates the process as well and leads to similar thermal pulsing. The relative amount of surface absorption versus volume absorption can strongly influence the heat flow and therefore the mass spectrum of the specimen. Thus it appears for very different reasons that all materials behave similarly in response to laser pulsing in atom probe tomography.

1. Introduction

Atom probe tomography (APT) uses time-of-flight (ToF) mass spectroscopy for elemental identification. In order to measure time of flight, a well-defined departure time must be induced for an ion. This implies pulsing the field evaporation process. Since field evaporation is an Arrhenius process, it may be pulsed by pulsing the relevant terms in the expression for field evaporation rate, Eq. (1) [1]:

$$\boldsymbol{R} \propto \boldsymbol{e}^{-\frac{Q_n}{kT}} \tag{1}$$

where $\boldsymbol{R}$ is the evaporation rate, Q_n is the activation energy barrier for field evaporation of an n-fold charged ion, k is the Boltzmann constant, and T is the specimen apex temperature. In this model, field evaporation is viewed as thermal activation over an energy barrier.

$\boldsymbol{R}$ may be pulsed by modulating Q_n or T in Eq. (1). Pulsing of Q_n is known as field pulsing and pulsing of T is known as thermal pulsing. Field pulsing in APT is common for metals and other highly conductive materials. It is accomplished by pulsing the voltage applied to the specimen in an atom probe. Q_n depends on the local electric field and goes to zero at a high field which is called the zero-Q evaporation field [1]. This mode of operation of the atom probe is not the subject of this paper, however, and will not be discussed further.

We are here concerned with methods of pulsing the field evaporation rate that do not involve pulsing of the applied voltage on the specimen. This is not to say that we are disinterested in ways to pulse the electric field at the surface of the specimen. In some of the methods considered below, we consider whether the field may be pulsed by, for example, the electric field of the photon pulse. We note that pulsing might be mediated by any pulsed energy source. For example, electron beam pulsing of atom probes has been considered in some detail previously [2,3] but it has not been demonstrated to work experimentally and its feasibility remains an open question. We will consider here only pulsed laser sources of energy as these are the only ones being applied today and are the only practical solution apparent in the immediate future.

Given this backdrop, it is instructive to consider laser pulsing of a strong dielectric like Al_2O_3. As a dielectric, one might expect that it is not possible to apply an electric field to its apex since the fields should penetrate through to some conducting surface. If that is not challenging enough to explain, we also note that it is possible to illuminate the specimen with pulses of 3 eV photons and produce high quality pulsed field evaporation. But Al_2O_3 has a 9 eV band gap and the photons should pass right through. Why then is it possible to pulse field evaporate Al_2O_3 specimens? This paper is an attempt to explain this and the pulsed field evaporation of all materials with laser energy.

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2. Athermal versus thermal pulsing

If a pulsed energy source induces a momentary rise in evaporation rate without a significant rise in the specimen temperature, it is termed athermal. The crucial experimental difference between athermal and thermal pulsing mechanisms is the potential temporal width, Δt, of the evaporation pulse. By definition, any athermal pulse should yield elevated evaporation rates only while the laser pulse is on. Since laser pulses can be quite short (<10 ps) compared with typical ion flight times (hundreds of ns), athermal pulsing has potential for very high mass resolving power, $\frac{m}{\Delta m} = \frac{t}{2\Delta t}$, where m is the ion mass and t is the time of flight. The best atom probe instrumentation today achieves about 80 ps timing resolution overall (based on 40 ps timer chips). If field evaporation were pulsed athermally with 10 ps pulses or shorter, and in the absence of any spread in the energy of the ions, all peaks in a time spectrum would be Gaussian in shape and have a full width at half maximum (FWHM) of about 80 ps. Energy spreads of about 1 eV have been measured for field evaporated ions from a range of materials which has an insignificant effect on peak shapes. The finest peak width known to these authors is about 115 ps from an ideal aluminum specimen. Most peaks are closer to 200 to 500 ps in width. Thus from this standpoint alone, there has never been a convincing demonstration of athermal field evaporation in a standard atom probe experiment.

There have been efforts to determine whether field evaporation pulsing occurs by an energy absorption mechanism or some athermal mechanism. Tsong et al. [4] found no significant contribution of athermal mechanisms to the overall measured evaporation rate of metals which might support other theories of field evaporation mechanisms, such as photoionization and field enhancement [5]. Some evidence was found that photoexcitation may accompany the dominant thermal evaporation of semiconductor species in PLAP experiments [4]. Direct photoionization of atoms on the surface of a specimen under high electric field would seem to lead to field evaporation. However, the lifetime of ions on the surface is on the order of 30 fs for metals which, even under 10^{10} V m^{-1} field, is only enough time for an ion to move about 0.001 nm and therefore photoionization should not happen for metals. For dielectrics, the ion lifetime can be two orders of magnitude greater and photoionization might be sensible under these conditions [4].

Another potential athermal field evaporation pulsing mechanism is based on optical rectification [6,7]. In ultrashort laser pulses, the intensity can be very high and the electric field of the photon pulse is the square root of the intensity. This very high electric field can reach 10^{10} V m^{-1} which is the magnitude of the evaporation fields in atom probe tomography. However, this electric field is oscillating in space at very high frequency and is not oriented normal to a surface long enough to cause a field evaporation event. It is known that surface plasmons can act to rectify the alternating fields of a photon pulse [8]. In ultrashort laser pulses of high fluence then, the rectified electric field might be high enough to cause field evaporation. Since it is an athermal process, the time of departure spread should be equal to the laser pulse duration and peak widths of mass spectra would be much smaller than the timer precision which is not observed. This mechanism has not been shown to be present in any experiments [9–11] and is now considered to be insignificant in magnitude if it is even possible.

Tamura et al. [12] suggest an athermal evaporation mechanism for dielectrics based on hole accumulation near surface atoms. Holes would be created during the laser pulse by photo-excitation and the energetic electrons would be conducted away by surface conduction. Using electric field modeling, they tie hole accumulation from laser pulsing to experimental work [13] that shows changes in magnification in field ion images when the laser is on. Their proposal is that accumulation of holes lowers that activation barrier for field evaporation until the zero-Q field is achieved. The relative magnitude of this mechanism and any concomitant thermal pulsing have not been evaluated and timer-limited mass spectra have not been published. This mechanism may be feasible but it has not yet been demonstrated unequivocally to be operative.

Thus, to date, thermal pulsing of field evaporation is the only mechanism that is known to be operative in atom probe tomography experiments. The outstanding questions relate to the mechanisms of energy absorption, thermalization of the absorbed energy, and subsequent cooling of the specimen in a thermal pulse. For simplicity in the following treatment, we will consider three categories of materials in the continuum of electrical behavior; metals, semiconductors, and dielectrics.

3. Metals

3.1. Energy absorption

We shall consider first mechanisms by which lasers may deposit energy into a metal specimen. Photon energy in a pulsed laser beam may be absorbed either by electrons in a singular excitation or by plasmons in a collective excitation. In general, plasmon excitations require about 15 eV for bulk excitations and 10 eV for surface excitations. The highest energy photons currently employed for laser pulsing are on the order of 3 eV. Multiphoton absorption could occur in principle but it will be orders of magnitude less probable than the mechanisms discussed below and only becomes important for laser intensities that approach the ablation threshold for most materials. The laser intensity in atom probe experiments is about four orders of magnitude less than the ablation threshold. It has been shown for nanoparticles and nanorods that surface plasmon resonance can occur with UV and even visible light [14], so in some cases this effect must be considered. The data in Fig. 1 may be evidence of surface plasmon effects. This question of singular versus collective excitation is considered more fully below in the section titled Singular versus collective electron excitation. Thus, overall, electrons acting either singularly or collectively are the principal energy absorbing entity in materials illuminated by a laser.

Electrons absorb energy over a distance into a metal known as the optical skin depth, δ [5,16]. Once a single electron has absorbed energy, it is "hot" but the surrounding atoms are still "cold". A two-temperature system is created. The hot electrons (3 eV $\approx 10^4$ K) thermalize with the atoms creating phonons (heat) over thermalization times on the order of 0.5 to 10 ps [17,18]. During this time, the hot electrons may travel in the material a distance characterized by their diffusion length, L_D, which may be on the order of 20 times the optical skin depth [19]. After thermalization, the specimen apex region locally will be warmer and the maximum lattice temperature within the specimen will have been reached. Heat flow by conduction down the shank of the specimen cools the specimen apex region over the ensuing nanoseconds.

Moreover, due to different interference phenomena taking place during the interaction between optical radiation and a sub-wavelength specimen, the electromagnetic energy may not be absorbed homogeneously by the sample. On the one hand, in the case of a metallic specimen where the laser beam will be heavily absorbed near the surface, the interference pattern is analogous to the one analytically computed on a semi-infinite metallic plate [20]: it has a spatial period equal to the incident wavelength and can be observed mostly on the illuminated side of the specimen. Photons scattered from the apex of the specimen interfere with the primary laser beam and lead to periodic variations in the absorbed energy along the specimen. The first maximum is located at a fraction of