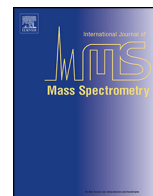




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Pulse shaping optimization for improving atom probe tomography

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ABSTRACT

We propose in this paper novel approach for improving mass resolution in atom probe tomography. Using conventional counter-electrode or microelectrode design, improved mass resolution at half, tenth and 1% of the mass peak maximum is predicted when shaping properly the voltage evaporation pulse. Using a numerical approach, it is shown that a flat top voltage pulse used to trigger the field evaporation with sharp front and leading edges associated with a short tip to counter electrode distance ($\approx 10 \mu\text{m}$) strongly minimizes the energy deficits of evaporated ions from the sample, so that energy compensation devices are not necessary to obtain high mass resolution.

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1. Introduction

In the 60s, Müller et al. transformed the field ion microscope (FIM) [1] into a powerful quantitative nano-analyzing technique by applying the concept of time-of-flight mass spectrometry [2] to a simple imaging technique [3,4]. Indeed, in atom probe, time-of-flight mass spectrometry enables to provide the elemental identities to atoms observed at the atomic scale in FIM. Since then, several generations of instruments have been developed from this principle and this technique named atom probe tomography (APT) is now a widely spread nanocharacterization technique. The basic principle of the technique is the atom-by-atom erosion of a sample by the physical mechanism of field evaporation. An intense electric field (in the range 10–60 V/nm), sufficient to pull-out the atoms of the surface in the form of ions, is produced at the sample surface by the application of a strong positive voltage V between the sample and a counter electrode. The sample is prepared as a sharply pointed needle with a hemispherical apex of about 50–100 nm in radius (R). The pointed nature of the sample enhances greatly the surface electric field F so that a few kV are generally sufficient to reach the required critical electric field (F_{EV}) ($F_{EV} = \frac{V}{kR}$, with k a constant in the range of 2–8, which depends on the specimen shape and the system geometry.) [5–9]. Ions emission can be triggered by short positive voltage pulses applied to the sample or negative voltage pulses applied to the counter electrode [10]. Time-of-flights are measured by calculating the delay time between the start time

(the triggering pulse) and the ion arrival time on a position sensitive detector placed more than 10cm in front of the sample.

One of the key performances of modern instrument is its mass resolving power. Sufficient mass resolution must be achieved to separate mass peaks even if the amplitude of close peaks is very different. High mass resolution at half maximum ($M/\Delta M > 1000$) is important, but more critically the smallest width of mass peak at ten percent, or even 1% of the maximum is of fundamental importance [11]. In voltage-pulsed atom probe, field evaporated ions leave the sample at slightly different times relative to the pulse maximum (start-time), because of the stochastic nature of the evaporation process [1]. This causes some ions of the same nature to acquire slightly smaller kinetic energies, and therefore slightly slower velocities compare to the peak maximum, resulting in a high mass tail in the mass spectrum. This effect degrades significantly the mass resolution. To overcome this problem, modern instruments are generally equipped with an energy compensation device (named reflectron) [12]. This electrostatic device uses a static electric field in a defined region of the ion path to reverse the direction of travel of the ions entering it. With the reflectron, one can substantially diminish spreads of flight times of the ions with the same mass-to-charge ratio caused by the spread in kinetic energy of these ions measured at the exit from the ion source. If mass spectra are greatly improved by this device, the detection efficiency of the instrument is degraded by the need of a mesh with fine line spacing to ensure a smooth potential variation along the path of ions and good ion optic performances [13].

To avoid this requirement, different devices were suggested to reduce the impact of energy spread on the mass spectrum. A slight improvement in the mass resolution was obtained in Scanning atom probe (SAP) [14] or local electrode atom probe (LEAP) [15]. In

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these instruments a reduced distance (in the micron scale) between the counter electrode and the sample is used. This enables to reduce significantly the voltage required for field evaporation, and better quality voltage pulser could be utilized.

The dual electrode design was proposed by Kelly et al. [11] for improving mass resolution in LEAP. By accelerating the evaporated ions to a greater total potential after the local extraction electrode, the energy spread will be relatively small to the total energy leading to an improvement in the final mass resolution. Some preliminary experiments [16] show that a better mass resolution could be achieved. However, the required post-acceleration field is so high that it will affect the field on the tip. The practical mass resolution improvement may be limited. Cerezo et al. [17] also utilizes a two-conductor micro-electrodes placed at near of the sample. The evaporated ions are accelerated and decelerated with an essentially constant pulse voltage, and thus the resultant energy deficit is small, giving an improvement in mass resolution. They show preliminary experimental and simulation results [18,19] confirming the improvement in mass resolution with the two-conductor electrodes. But, this technique strongly depends on the mass of ion and the shape of the voltage pulse.

The aforementioned methods provide different ways to reduce energy deficits with some deterrents. We propose in this paper, a new method that reduces from its source the relative amount of ions with energy deficits. We propose using square shape voltage pulses, with width at half maximum less than 1ns limiting time spread. A numerical model is used to show that fast rise and leading edges are necessary to improve the mass resolution of the technique. A simple device using optoelectronic switching is proposed in this article.

1.1. Origins of the mass resolution degradation

The mass over charge measurement of detected ions is directly associated with the measured time of flight (t_{of}), Fig. 1. This time t_{of} is defined as the time between the application of the voltage pulse and the moment when the impact is measured by the electronic system. In a simple approach, it is assumed that the ion acquires the potential energy $E = neV$ from the surface of the tip with no initial velocity, where V is total voltage between the tip and the counter-electrode, ne is the charge of ion. Assuming instantaneous acceleration of the ion, the time of flight can be given by:

$$\frac{1}{2} m \left(\frac{l}{t_{flight}} \right)^2 = neV \quad (1)$$

where l is the total flight distance. The mass to charge ratio will be given by:

$$\frac{m}{n} = kV \frac{t_{flight}^2}{l^2} \quad (2)$$

where $k = 0.193 \text{ m}^2 \text{ kV}^{-1} \mu\text{s}^{-2}$.

This calculation neglects the time varying shape of the evaporation pulse which takes place during the voltage pulse. Evaporation is triggered by the field pulse $F(t)$ induced by the voltage $V(t)$. Field evaporation is an atomistic physical mechanism, thermally assisted that can be modeled by an Arrhenius expression: (We refer the reader to the book of Michael K. Miller [21] Chapter 3 for a detailed explanation of Eqs. 1 and 3), the rate of generation K_{hr} is written as:

$$K_{hr} = A_{hr} \exp \left(-\frac{Q(F)}{K_B T} \right) \quad (3)$$

where A_{hr} being the field evaporation rate-constant pre-factor for high risk atoms, K_B the Boltzmann factor, T the temperature, and

$Q(F)$ the field evaporation activation energy depending on the surface electric field. The activation energy has the general form

$$Q(F) = C_1 \left(1 - \frac{F}{F_{EV}} \right)^l \quad (4)$$

where l is a constant, C_1 is an energy-like parameter and F_{EV} is the zero barrier evaporation field. We assume here that F is close to F_{EV} at the field pulse maximum. In the first approximation, the factor l is taken to 1, saying a linear relationship can be written. Considering the equation

$$F = \frac{V}{kR} \quad (5)$$

The maximum probability of the evaporation pulse K_{max} is assumed for $V(t=0) = V_{max} = V_0 + V_p$, with V_0 the standing voltage on the tip, and V_p the maximum amplitude of the voltage pulse. Considering $\alpha_p = V_p / (V_0 + V_p)$ is the pulse contribution, and assuming a simplified approach that $F = F_{EV}$ for $V = V_{max}$, $V(t)/V_{max} = (1 - \alpha_p) + \alpha_p f(t)$, with $f(t)$ the temporal shape of voltage pulse equal to 1 at $t=0$ and null far from $t=0$, see Fig. 2(a). Considering these expressions, the evaporation rate can be rewritten as

$$\frac{K(t)}{K_{max}} = \exp \left(-\alpha \left(1 - \frac{V(t)}{V_{max}} \right) \right) = \exp(-\alpha \alpha_p (1 - f(t))) \quad (6)$$

where $\alpha = \frac{C_1}{K_B T}$, T the temperature and K_B the Boltzmann's constant.

Considering $C_1 \sim 1 \text{ eV}$, $T \sim 100 \text{ K}$ and $l \sim 1$, α is about 100. Assuming a voltage pulse with a Gaussian shape $f(t) = e^{-\frac{t^2}{2\sigma^2}}$ with σ the standard deviation, this equation rewrites

$$\frac{K(t)}{K_{max}} = \exp \left(-\alpha \alpha_p \left(1 - \exp \left(-\frac{t^2}{2\sigma^2} \right) \right) \right) \quad (7)$$

Due to the large value of $\alpha \alpha_p (\approx 10 - 30)$, the evaporation rate strongly decreases with t . Only field value close to $t=0$ give rise to significant evaporation so that, we can approximate the expression to

$$\frac{K(t)}{K_{max}} \simeq \exp \left(-\alpha \alpha_p \left(\frac{t^2}{2\sigma^2} \right) \right) \quad (8)$$

For realistic values of α and α_p , the approximate evaporation rate agrees well with theoretical curve as shown in Fig. 2(a). For ion evaporating with a small delay t_D , the relative energy loss is $\delta_c = \alpha_p \left(\frac{t_D^2}{2\sigma^2} \right)$. The number of ions evaporating for $\delta < \delta_c$ is

$$N(\delta_c) = K_{max} \int_{-t_D}^{t_D} \exp \left(-\alpha \alpha_p \left(\frac{t^2}{2\sigma^2} \right) \right) dt \quad (9)$$

So that

$$N(\delta_c) = 2K_{max} \sigma \left(\frac{2}{\alpha \alpha_p} \right)^{1/2} \int_0^{(\alpha \delta_c)^{1/2}} \exp(-t^2) dt \quad (10)$$

This simplifies to

$$\frac{N(\delta_c)}{N_{total}} = \text{erf}[(\alpha \delta_c)^{1/2}] \quad (11)$$

where N_{total} is the total number of evaporated ion per pulse. Note that the shape of the distribution is only dependent on α (Fig. 2(b)). The voltage pulse fraction and the voltage pulse duration do not have any influence on the energy distribution (assuming that the pulse fraction not too small, and the sample temperature not too high). Table 1 shows that the low temperature can reduce the energy deficit and thus improve the mass resolution. Note that this study neglects the energy deficit induced by the process of ionization described by [22].

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