New time-of-flight electronics for atom-probe field-ion microscopy

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We present new time-of-flight electronics for atom-probe field-ion microscopy that is based on the LeCroy 2277/EXP2 time-to-digital converter (TDC) and is significantly superior to the commonly used LeCroy 4208 TDC. The maximum number of ions detected for each cycle is increased, the electronics dead time is decreased, and the pulse width from the Phillips Scientific 6904 discriminator is measured. The LeCroy 2277/EXP2 TDC records up to 128 ions per field evaporation pulse as opposed to a maximum of eight ions for a single LeCroy 4208 TDC. The dead time is reduced by increasing the pulse pair resolution, in the multihit mode of the TDC, from 7.3 to 3.3 ns. The LeCroy 2277/EXP2 TDC has both leading and trailing edge detection capability, allowing us to measure the pulse width generated by the Phillips Scientific 6904 discriminator. Combining the pulse width measurement capability with the updating capability of the Phillips Scientific 6904 discriminator, in which the discriminator extends the output pulse width by the time difference between two closely spaced (<2 ns) pulses, we resolve two ions arriving within 2 ns of each other. With these improvements, we find that 66% of the total number of multiply field-evaporated ions arriving with a pulse separation of up to 8 ns are incorrectly counted as a single ion. The percentage of multiply field-evaporated ions occurring with a pulse separation of 2 ns is 6%.

I. INTRODUCTION

Atom-probe field-ion microscopy (APFIM) is an atomic resolution chemical analysis technique capable of quantitatively determining the chemistry of materials on an atom-by-atom basis if some simple calibration experiments are first performed.1–9 The APFIM technique is described in great detail elsewhere10–19 and only a precis is presented here. It is based on the principle of the pulsed field-evaporation of ions from a sharply pointed tip maintained at high voltage (V dc), by superimposing a pulse voltage (VP) on top of V dc; VP is normally a constant fraction of V dc. ~10–25 ns wide voltage pulse raises the electric field—Vdc /vp—above the threshold evaporation field for the particular material being studied, resulting in the evaporation of ions from a tip. For a metal, for example, the Debye screening length is less than 0.1 nm, hence the electric field is highly localized in the surface atoms. Furthermore, for a particular crystallographic plane the electric field is highest at the edge of an atomic plane and therefore ions field evaporate from this edge inward. In this manner each individual atomic plane can be dissected on an atom-by-atom basis. The pulsed field-evaporated ions are accelerated by the high electric field down a straight drift tube or into a reflectron lens17 where they are detected by a chevron channel electron multiplier array particle detector;16 the ions reach their terminal velocity in a few tip radii (150 nm) and then move at constant velocity over a drift distance that is approximately 2200 nm in our straight time-of-flight atom probe and approximately 1500 mm in our atom probe with a reflectron lens. Figure 1 is a schematic diagram of the atom-probe electronics with a straight time-of-flight tube; it is noted that the same electronics are also utilized for an atom probe with a reflectron lens.16

By measuring the time-of-flight and drift length, the mass-to-charge state ratio (m/ne)—where m is the mass, n the charge state and e the charge on an electron—is calculated for each pulsed field-evaporated ion. The times-of-flight are measured employing a time-to-digital converter (TDC); the most widely used one at present is a LeCroy 4208 with eight channels. The TDC clocks are started simultaneously with the generation of a pulse voltage. When an ion hits the chevron detector it generates a voltage pulse that is amplified and then passed through a wide band discriminator; this voltage pulse then stops one clock, corresponding to one channel, and the measured time-of-flight is then sent to a computer via an IEEE 488 general purpose interface bus; our atom probe employs a Macintosh IIx computer to record and analyze the times-of-flight while simultaneously collecting data.20 The timing relationships of the important signals of the new atom-probe time-of-flight electronics are exhibited in Fig. 2. We are currently employing an active window of 24.6 μs (see Fig. 2), although the maximum value for a LeCroy 2277 TDC is 64 μs: the latter value is more than adequate for atom-probe microscopy.

The values of the ratio VP/V dc, the field-evaporation rate and the pulse frequency are specified by an operator using a dialog box in the atom-probe operating system software. An algorithm in the operating system software automatically sets the values of VP and V dc necessary to achieve the specified field-evaporation rate; in this manner it is possible to detect more than 20 000 ions in a single run without the failure of an atom probe specimen. Our present time-of-flight electronics are based on two LeCroy 4208 TDCs running in parallel, which limits us to recording up to eight ion times-of-flight per TDC for a maximum of 16 ions. The LeCroy 4208 TDC clocks are stopped by the leading edges of the ion pulse.
FIG. 1. A schematic diagram exhibiting an atom-probe field-ion microscope with a straight time-of-flight tube. Ions that are pulsed field-evaporated from an atomically sharp tip are accelerated to their terminal velocity in a few tip radii and pass through the probe hole of a channel electron multiplier array that is 40–80 mm from the tip. The total drift length from the tip to the chevron channel electron multiplier array detector is ~2200 mm. The output voltage pulses from the chevron detector are first sent to a Phillips Scientific 6954 amplifier and then to a Phillips Scientific 6904 discriminator. The output of the discriminator is then directed to the LeCroy 2277/EXP2. The processes of the initiation of a pulse and the calculation of the mass-to-charge state ratio of a detected ion are performed by a Macintosh IIfx computer. The computer controls and analyzes the data in real time, and operation of the atom-probe does not require the presence of an operator once a run has commenced.

II. ELECTRONIC ARCHITECTURE

A LeCroy 2277 TDC has 32 clock channels which record up to 16 times of flight per channel for a total of 512 times. It has both leading and trailing edge detection capability, giving us the ability to measure pulse widths. The LeCroy 2277 TDC features a pipelined multihit operation, in which the last 16 times per channel are retained, and all previously recorded times are lost. It has a resolution of 1 ns, a pulse pair resolution of 30 ns, and a minimum detectable pulse width of 15 ns. These specifications are improved with the addition of a LeCroy 2277 EXP2 expander board. The LeCroy EXP2 expander board reduces the number of inputs from 32 to 2, and features fast flip-flops that distribute the recorded times-of-flight among the 32 channels that are tied together. The LeCroy EXP2 expander board increases the pulse pair resolution to 2 ns with a minimum pulse width detection limit of 1 ns.

In comparison to the LeCroy 4208 TDC, the incorporation of a LeCroy 2277 TDC with a 2277 EXP2 expander board, hereafter called a LeCroy 2277/EXP2 TDC, improves the pulse pair resolution from 3 to 2 ns, and the minimum detectable pulse width from 4 to 1 ns. A comparison of the LeCroy 4208 TDC vs the LeCroy 2277/EXP2 TDC is given in Table I. A Phillips Scientific 6904 discriminator21 "thresholds" the output signal from a Phillips Scientific 6954 amplifier22 and outputs a pulse when the signal is above a threshold value. The discriminator is used to eliminate background noise. The width of the pulses from the discriminator can be continuously adjusted from 2 to 50 ns and there is a

![Diagram of the electronic architecture](image)

FIG. 2. The timing relationships between the important signals of the time-of-flight electronics. The signal that initiates the cycle is the trigger pulse with a continuously variable repetition rate between 5 and 150 Hz. The rate is a user defined variable in the atom-probe operating system software. The maximum active window of the LeCroy 2277 TDC is 64 μs, although we are currently using 24.6 μs.

<table>
<thead>
<tr>
<th>Table I. The main characteristics of the LeCroy 4208 TDC, the LeCroy 2277 TDC, the LeCroy 2277 TDC with an EXP2 expander board, and a Phillips Scientific 6904 discriminator.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LeCroy 4208 TDC</strong></td>
</tr>
<tr>
<td>Resolution (ns)</td>
</tr>
<tr>
<td>Minimum pulse width (ns)</td>
</tr>
<tr>
<td>Pulse pair resolution (ns)*</td>
</tr>
<tr>
<td>Number of channels</td>
</tr>
<tr>
<td>Number of inputs</td>
</tr>
</tbody>
</table>

*This is the pulse pair resolution in the multihit mode.
This signal then erroneously interpreted as due to the wide pulses with 1.3 ns between pulses. The maximum resolution of wide pulses and a pulse pair resolution of 7.3 ns from the$
$LeCroy 4208 TDC, and this discriminator limits our electronics to a 3.3 ns pulse pair resolution. This resolution is better than the previous configuration we employed with two LeCroy 4208 TDCs in parallel. Although the maximum resolution for a LeCroy 4208 TDC is 5.3 ns (4 ns plus 1.3 ns dead time) in the multihit mode, our previous setup used 6 ns wide pulses and a pulse pair resolution of 7.3 ns from the discriminator to ensure that the LeCroy 4208 TDCs were stopped. A comparison of the main features of our new and old electronics is displayed in Table II. At present we are using one input of 16 channels, giving us a detection capability of 128 times-of-flight per pulse of both 128 leading and trailing edges per pulse—we hope to utilize both inputs soon. This increases the number of recorded ions per pulse by a factor of eight—up from 16 ions per pulse for two LeCroy 4208 TDCs running in parallel.

### III. DOUBLE-ION EVENT DETECTION: THEORY

If several ions are field-evaporated simultaneously by the application of a single field-evaporation pulse and if each ion has a different mass-to-charge state ratio, then each ion is detected and an exact quantitative chemical analysis is obtained. If, however, two or more ions with the same mass-to-charge state ratio field evaporate at the same instant of time, then they can all arrive simultaneously at the chevron particle detector, and only a single output voltage is created. This signal is then erroneously interpreted as due to the arrival of a single ion and it results in a false determination of the chemical composition or isotopic distribution. Previous publications address this double ion or "pile-up" effect by: (a) altering the ion detection method of the Chevron detector by dividing the detector into four independent sectors with equal areas; (b) by tilting the detector by 30° to introduce an artificial spread in flight times; or (c) statistical correction of the collected data. These approaches do not directly address the problem of the dead time in the electronics. In reality, two ions probably never field evaporate at precisely the same instant of time, hence the ability of the new atom-probe electronics to detect two ions that are temporarily very closely spaced and affects our capability to observe so-called double-ion events.

Before proceeding to examine some experimental data that illustrates this point we present a simple theoretical model that amplifies the importance of these double-ion events. Consider a material that contains two species—A and B—and let $C_a$ and $C_b$ equal their atomic fractions. In the case of different charge states or isotopes, the concentration of each species is simply determined by the relative population of each species after field evaporation. Assume that exactly two ions field evaporate for each pulsed field-evaporation event. Then there are three possible field-evaporation products—two A ions, two B ions, or one A ion and one B ion. If, however, two A ions or two B ions field evaporate simultaneously then they are detected as one or one B ion. The probability of formation for each field evaporation event is displayed in Table III. The sum of the individual probabilities is $(C_a^2 + C_b^2) = 1$ as required. After $N$ pulsed field-evaporation events—$2N$ total ions evaporated—the number of A ions detected is equal to $N(C_a^2 + 2C_aC_b)$, the number of B ions detected is equal to $N(C_b^2 + 2C_aC_b)$, and the total number of ions detected is equal to $N(1 + 2C_aC_b)$. It is emphasized that the total number of ions detected is less than the number of ions pulsed field-evaporated—$2N$. This implies that the measured concentrations of A and B, $C_a^*$ and $C_b^*$, respectively, are given by

$$C_a^* = \frac{(C_a^2 + 2C_aC_b)}{(1 + 2C_aC_b)} \quad (1a)$$

and

$$C_b^* = \frac{(C_b^2 + 2C_aC_b)}{(1 + 2C_aC_b)}. \quad (1b)$$

The ratio of Eq. (1a) to Eq. (1b) is given by

$$C_b^*/C_a^* = \frac{(C_b^2 + 2C_aC_b)}{(C_a^2 + 2C_aC_b)}. \quad (2)$$

If $C_b$ is much less than $C_a$ then the following inequality is obtained:

$$(C_b^*/C_a^*) > (C_b/C_a). \quad (3)$$

Therefore, the measured concentration of solute ($C_b^*$) is greater than the actual concentration of solute ($C_b$). For a dilute alloy of $B$ in $A$—$C_b^{\infty} < C_a$—the measured concentration of $B$ approaches twice the actual concentration. That is, $C_b^*$ approaches $2C_b$, and the resulting error is 100%. Finally, the ratio ($\beta$) of ions detected to ions field evaporated is given by the following relation:

$$\beta = (0.5 + C_b/C_a). \quad (4)$$

The range of $\beta$ in Eq. (4) is $0.5 \leq \beta \leq 0.75$.

### TABLE II. A comparison of the main characteristics of our prior time-of-flight electronics system based on two LeCroy 4208 with our new time-of-flight electronics system based on the LeCroy 2277/EXP2

<table>
<thead>
<tr>
<th></th>
<th>Previous setup:</th>
<th>New setup:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>two LeCroy 4208b</td>
<td>LeCroy 2277/EXP2b</td>
</tr>
<tr>
<td>Pulse width (ns)</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Pulse pair resolution (ns)$^a$</td>
<td>7.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Number of channels</td>
<td>16</td>
<td>256</td>
</tr>
<tr>
<td>Maximum number of ions</td>
<td>16</td>
<td>128</td>
</tr>
<tr>
<td>Number of inputs</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$This is the pulse pair resolution in the multihit mode.

$^b$With a Phillips Scientific 6954 amplifier and a Phillips Scientific 6904 discriminator.

### TABLE III. The probabilities for forming different pulsed field-evaporation events and the corresponding number of ions detected.

<table>
<thead>
<tr>
<th>Evaporation event</th>
<th>Probability</th>
<th>Number of ions detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A</td>
<td>$C_a^2$</td>
<td>1A</td>
</tr>
<tr>
<td>2B</td>
<td>$C_b^2$</td>
<td>1B</td>
</tr>
<tr>
<td>1A + 1B</td>
<td>$2C_aC_b$</td>
<td>1A + 1B</td>
</tr>
</tbody>
</table>
For a multicomponent alloy in which two ions field evaporate simultaneously, the measured concentration of component \( i \) is given by the equation

\[
C_i^s = \frac{C_i^2 + 2C_i(1-C_i)}{1 + \sum_i C_i(1-C_i)}. \quad (5)
\]

For this case the value of \( \beta \) is given by the expression

\[
\beta = 0.5 \left( 1 + \sum_i C_i(1-C_i) \right). \quad (6)
\]

The range of \( \beta \) in Eq. (6) is \( 0.5 \leq \beta \leq 0.5 + (S-1)/(2S) \), where \( S \) is the number of components in the alloy.

From the analyses presented in this section it is clear that it is important to establish whether a significant number of the ion events detected is in reality due to two ions being simultaneously detected. This question is addressed in the next section, where we demonstrate experimentally that if two ions are field evaporated with a time difference of greater than 2 ns, then they are detected as two separate events and no error occurs. We also demonstrate that the fraction of ions field evaporated with a time difference of less than 2 ns is quite small.

IV. DOUBLE-ION EVENT DETECTION: EXPERIMENT

With this new electronic configuration, we now address the question of double-ion event detection from an experimental point of view. Experimentally, a double-ion event is defined as a second ion that occurs within 2 ns of the first. When two ions occur within 2 ns of each other, the Philips Scientific 6904 discriminator extends its output pulse by the difference in times between the first and second pulses. We use the LeCroy 2277/EXP2 TDC to measure pulse widths from the discriminator. No pulses are detected during the 1.3 ns dead time. By defining a double hit as a pulse width that is greater than 4 ns wide, we directly resolve two ions occurring within 2 ns of each other. Double-ion events are recorded as two ions with the same time-of-flight. Note that this method does not take into account triple- or higher-order multiple-ion events, and these events, if they should occur, are treated as double-ion events.

We now consider a data set consisting of 9793 ion events; the total number of field-evaporation pulses was 608 178, implying an ion per pulse efficiency of 1.61%. The ions are obtained from an internally oxidized Ag-1.62 at. % Cd alloy employing a straight, non-energy compensating atom-probe field-ion microscope. The data is plotted in Fig. 3 in the form of a histogram of the number of ion events versus the time separation between two ions in ns. The number of ion events occurring within 2 ns of each other represents 6% of the number of ions occurring within 8 ns of each other; these are the nine events in the first bin. We note that the LeCroy 4208 TDCs would have missed the occurrence of the second ion when the separation is less than 7.3 ns, which is the maximum resolution in our previous setup. Thus, 97 ions would have been missed by the LeCroy 4208 TDC, or 66% of the total number of ions arriving within 8 ns of each other. Using the LeCroy 2277/EXP2 we detect the ions that arrive with time separations of less than 8 ns. This represents a 200% increase in detection efficiency.

For the future, in order to eliminate losses due to the discriminator dead time, it is proposed that two discriminators be used in parallel. Each discriminator is tied to a 16 channel input of the LeCroy 2277/EXP2 TDC. A 500 MHz flip-flop is required to change the output from one discriminator to another. The switching time would be 2 ns, thus activating the second discriminator during the 1.3 ns dead time of the first discriminator, and vice versa. This configuration would also allow us to utilize the second channel of the LeCroy 2277/EXP2 TDC, thereby increasing our maximum number of recorded times of flight to 256 per field evaporation pulse. To the best of our knowledge, no such switching mechanism is presently commercially available.

V. OVERFLOW ERRORS

As the occurrence of more than 16 ions resulting from one field evaporation pulse is not uncommon when field evaporating through multiphase materials, for example, oxide or carbide precipitates in metals there is a possibility that ions with long times-of-flight (and therefore large mass-to-charge ratios) are not recorded, and hence the composition analysis is weighted toward ions with smaller mass-to-charge ratios. This occurs because the small mass-to-charge state ratios are recorded first, thereby filling all 16 channels of the two LeCroy 4208 TDCs before the arrival of ions with large mass-to-charge state ratios. In an atom-probe analysis where the evaporation rate is such that the occurrence of greater than 16 ions per pulse is frequent, the measured compositions will be incorrect. This is because ions with small mass-to-charge state ratios are the ones that are predominantly measured. With our new electronics, we increase the overflow maximum to 128 ions per pulse. In the case of a LeCroy 2277 TDC, unlike a LeCroy 4208 TDC, an overflow of greater than 128 ions gives composition errors weighted...
toward large mass-to-charge state ratios. This occurs because the LeCroy 2277 TDC features an overflow stack in which the initial recorded times are pushed off the stack and the last 16 times of flight are retained. This favors longer times-of-flight rather than shorter times-of-flights. The compositions of ions with small mass-to-charge state ratios are thus incorrectly measured. The field evaporation rate can be controlled such that events greater than 128 ions per pulse occur infrequently—as compared to greater than 16 ions per pulse—even when the interfacial regions of two disparate materials are encountered.

In conclusion, the atom-probe time-of-flight electronics based on the LeCroy 2277/EXP2 TDC has improved the pulse pair resolution to 300 MHz, enabling us to resolve the arrival of two ions with a temporal spacing of less than 2 ns between them, and increased the TDC overflow maximum to 128 ions per pulse.

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20. The Macintosh IIfx is a 40 MHz computer containing 20 MBytes of RAM, a 240 MByte hard disc, a National Instruments NB-GPIB interface board to communicate with the CAMAC crate, and a National Instruments NB-MIO-16 board to control the high-voltage power supplies and the triggering of the high-voltage pulser.
21. The Philips Scientific 6904 discriminator has a 300 MHz continuous cycle rate. The discriminator has a continuously variable threshold from −25 mV to −1 V. It generates NIM pulses with a continuous adjustment of the width from 2—50 ns and a dead time of 1.3 ns between pulses. It features an updating capability, in that the output pulse is extended by the difference in times between the two input pulses, if a second pulse occurs before the end of the output pulse.
22. The Philips Scientific 6954 is a low noise inverting amplifier with a gain of 20 and a wideband performance up to 1 GHz.
23. The assumption is made that a detector pulse-height analysis is not performed. If the height of the voltage output by the chevron detector is proportional to the number of ions striking the detector simultaneously, an analysis of the pulse-height distribution could in principle be made. No evidence presently exists demonstrating that there is a proportionality between pulse height and the number of incident ions. On the contrary, evidence exists (see Refs. 24—26) that indicates a very broad pulse-height distribution results from a single incident ion. This suggests that establishing an accurate and useful proportionality between the number of incident ions the detector pulse height would be difficult.