A Standards-based Approach to Dopant Quantification Using Atom Probe Tomography

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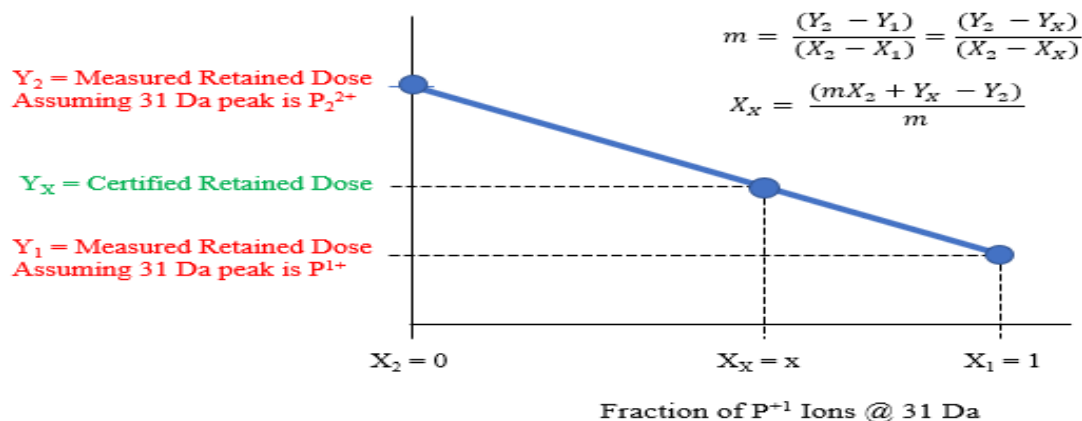*Corresponding author: karen.derocher@nist.gov

The continuous push to miniaturize semiconductor devices into the sub-5 nm regime has created many challenges in characterizing these materials [1]. One such challenge is spatially resolving the distribution of dopant atoms, an understanding of which is necessary to ensure device quality and performance.

Atom probe tomography (APT) has emerged as a valuable technique to study the chemistry and structure of semiconductor devices with features on the nanometer length scale [2, 3, 4]. In APT, a needle-shaped specimen is subjected to a high electric field and repeated energy pulses (either thermal or voltage), causing atoms or clusters of atoms on the apex of the tip to ionize and evaporate from the tip [5, 6]. The ions are accelerated in the electric field and directed towards a 2-dimensional position sensitive detector. The identity of the ion is determined based on its time of flight and, coupled with positional information also recorded by the detector, a 3D reconstruction of the sample is created. This technique produces detailed, chemical information with sensitivity in the range of 10's of µg/g. However, it has been established that the chemical quantification can be biased by experimental conditions that affect the electric field in which the ions are evaporating (e.g., laser pulse energy) [7, 8]. A specific example of this occurs in phosphorous (P) doped silicon (Si) where P evaporates as different ion species depending on the applied electric field. We hypothesize this is further complicated by both P^+ and P_2^{2+} contributing signal to the peak at 31 Da, making quantification difficult. Since P is mono-isotopic, the conventional approach of using natural isotope abundances as an aid for ion species identification and peak decomposition cannot be used to determine the contributions of P^+ and P_2^{2+} to the 31 Da peak. Using a reference material with a known retained dose of P (NIST SRM 2133, P implant in Si depth profile standard, [9]), we can calculate the fractions of P^+ and P_2^{2+} in the 31 Da peak with the approach outlined in Figure 1. By performing similar analyses under a variety of applied field conditions, a calibration curve is generated for P in Si measurements.

An FEI Helios NanoLab 660 FIB/SEM is used to prepare sample tips according to established procedures [10, 11]. The tips are then transferred to a local electrode atom probe (LEAP) 4000X Si (CAMECA Inc.) for analysis. In the LEAP, data is collected under ultra-high vacuum pressures ($< 1.2 \times 10^{-8}$ Pa) using a 355 nm wavelength UV laser pulsed at a rate of 500 kHz. To gather data across a variety of applied field conditions, multiple laser pulse energies are utilized. After calculating the calibration curve using data from the SRM, a well characterized sample of Si doped with a known concentration of P is used as a benchmark sample to assess the validity of our measurement methodology.

While standards-based analyses are common in many of the quantitative analytical methods used to determine chemical composition, reference materials are generally not employed in APT quantitative analyses. The present study on P-doped Si materials can demonstrate the use of reference materials to significantly improve the accuracy of these quantitative analyses conducted in the atom probe. Preliminary results indicate accuracy gains of up to 25% in terms of relative error [relative error = 100 *

(measured value-accepted value) / accepted value], over traditional non-standards-based methods, may be achieved. Looking forward, we plan to apply a similar measurement strategy to improve APT analysis accuracy in other materials systems [11].

$$m = \frac{(Y_2 - Y_1)}{(X_2 - X_1)} = \frac{(Y_2 - Y_x)}{(X_2 - X_x)}$$

$$X_x = \frac{(mX_2 + Y_x - Y_2)}{m}$$

Y_2 = Measured Retained Dose Assuming 31 Da peak is P_2^{2+}

Y_X = Certified Retained Dose

Y_1 = Measured Retained Dose Assuming 31 Da peak is P^{1+}

$X_2 = 0$ $X_X = x$ $X_1 = 1$

Fraction of P^{+1} Ions @ 31 Da

Figure 1. Schematic representation of deconvolution of 31 Da peak using a standard reference material. The two endpoints of the line represent the retained dose of P assuming the peak at 31 Da is either entirely P_2^{2+} (left) or entirely P^+ (right). Using the known retained dose of the reference material, the fraction of each ion type can then be determined.

References:

[1] M Fuechsle et al., Nature Nanotechnology **7** (2012), p. 242. doi: 10.1038/nnano.2012.21
[2] JP Barnes et al., Scripta Materialia **148** (2018), p. 91. doi: 10.1016/j.scriptamat.2017.05.012
[3] AD Giddings et al., Scripta Materialia **148** (2018), p. 82-90. doi: 10.1016/j.scriptamat.2017.09.004
[4] MA Khan, SP Ringer and R Zheng, Advanced Materials Interfaces **3** (2016). doi: 10.1002/admi.201500713
[5] DJ Larson et al. in "Local Electrode Atom Probe Tomography: A User's Guide", (Springer, New York) p. 29. doi: 10.1007/978-1-4614-8721-0
[6] DN Seidman and K Stiller, MRS Bulletin **34** (2009), p. 717. doi: 10.1557/mrs2009.194
[7] RJH Morris et al., Journal of Vacuum Science & Technology B **36** (2018), p. 03F130. doi: 10.1116/1.5019693
[8] F Meisenkothen et al., Ultramicroscopy **159**(1) (2015), p. 101. doi: 10.1016/j.ultramic.2015.07.009
[9] DS Simmons et al., Journal of Vacuum Science and Technology B **25** (2007), p. 1365. doi: 10.1116/1.2759937
[10] K Thompson et al., Ultramicroscopy **107** (2007), p. 131. doi: 10.1016/j.ultramic.2006.06.008
[11] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.