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Gaussian kernel density functions for compositional quantification in atom probe tomography

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ABSTRACT

Atom probe tomography (APT) has the ability to identify the nature and position of single atoms in a material with an almost 3D atomic resolution. However, the quantification of the material composition requires an appropriate treatment of the discrete APT data. When the amount of atoms selected to quantify the composition is relatively small, the spatial resolution is enhanced but the statistical error worsens. Conversely, the increase in the number of atoms considered reduces the spatial resolution, but improving the statistics. We have developed a methodology to reach an optimum equilibrium between the positional and the statistical error in an unsupervised form using Gaussian Kernel density functions. The validity of the method has been tested using APT simulated data of semiconductor materials. It has been proved that the chemical quantification in these materials requires the appropriate selection of the smoothing parameter, obtained without user intervention. In addition, the results have been compared to the usual techniques for composition measurement from APT data (voxelization and proximity histograms), showing better precision for high spatial resolution. This work supplies a data driven methodology based in Gaussian Kernel density functions for the accurate quantification of the composition from APT data.

1. Introduction

Atom probe tomography is an analytical technique where the ions are extracted from a needle-shaped specimen with high electrical voltage or laser pulses. After the reconstruction of the obtained information, the position and the nature of the ions (from several thousand ions to dozens of millions) are obtained. APT data can provide information on particular features of a material such as grain boundaries [1], precipitates [2], clustering [3] or dislocations [4]. Frequently, a visual examination allows an estimation of the size, shape or preferred orientation of these nanofeatures. However, when quantitative information about the composition of the material is needed, the data treatment is a further challenge. Accurate parameters for this analysis obtained independently of the user need to be selected to ensure that small changes are truthfully considered.

Many strategies have been developed to quantify the composition of materials from APT data, such as the atom-to-atom strategies [5,6], methodologies to find the nearest neighbors distribution [7] or the use of cluster identification algorithms [8–11]. Another strategy consists on including a 3D grid in the APT data (voxelization) for counting the number of atoms in each region [12] or for analyzing the frequency distribution of the atoms [13]. Nowadays, this is the most usual strategy for extracting quantitative information from the APT data.

The voxelization subdivides the entire volume of data into small individual regions, called blocks or voxels. The atomic content of each voxel is measured and visualization techniques as isoconcentration surfaces [14], concentration profiles [15] or proximity histograms [16,17] are used. Two main variables are used in this method: the block size and the transfer function. Regarding the block size, there are no unified criteria on the best procedure to choose this parameter [18,19] and because of this the effectiveness of this method is reduced. On the other hand, the transfer function is a smoothing parameter that is often introduced to reduce the statistical fluctuations, e. g., how the contribution of each atom to each block is [20]. The shape and size of the transfer function markedly influences the measurement [12,20]. Gaussian kernel functions for smoothing the data [21,22] and for the adjustment of the voxel size [23] can be used during the voxelization. A nonparametric approach for the Gaussian kernel functions is the density estimation [24], as used by Srinivasan to determine the optimum voxel size [23]. However, the Gaussian kernel functions used as a density

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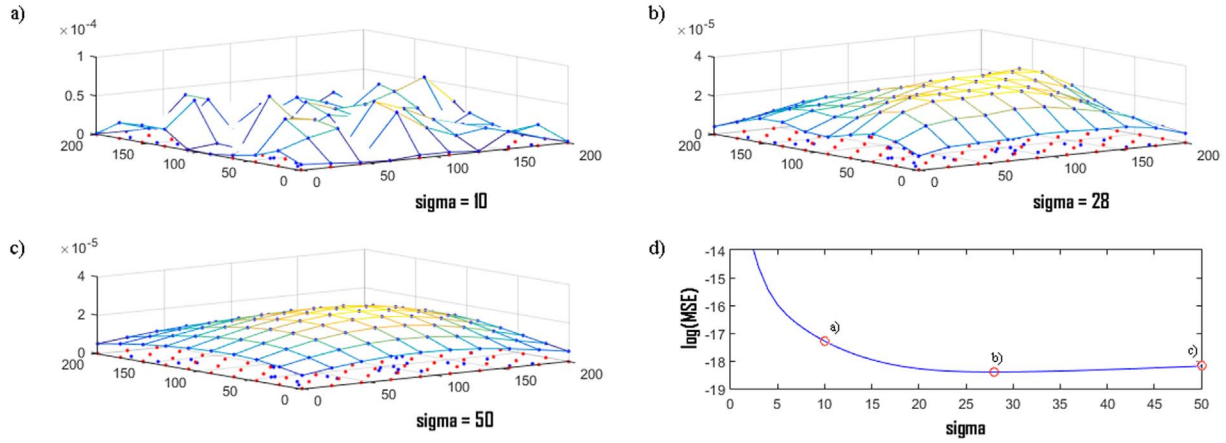

Fig. 1. Simulated data. a) $In_xGa_{1-x}As$ alloy where the In composition is modulated in *Z*-axis. b) GaAs/InAs/GaAs Quantum Well structure.

estimator can also be useful for acquiring the contribution of each atom to the composition of the material without the need to sub-divide the material into voxels. This approach is investigated in the present paper.

In some materials, the accurate chemical quantification is especially important because subtle chemical changes may result in the modification of the material properties. This is the case of the semiconductors materials, where information at atomic scale of heterostructures consisting on Quantum Wells [25,26] or Quantum Dots [27,28] is required to understand their functional properties. In semiconductor materials, very small compositional variations may change or prevent the desired response. For example, in InGaN layers composition fluctuations in the alloy have been suggested to cause charge carriers localization [29]. In GaAs/AlGaAs nanowires, chemical fluctuations have been found to produce sharp photoluminescence lines but below the AlGaAs band edge [30].

In this work, a methodology for obtaining quantitative information of the composition from APT data using Gaussian kernel density functions is shown. The validity of the method is assessed using simulated APT data of semiconductor materials, where sharp and soft compositional gradients are included. The deviations of the obtained results from the designed simulations are discussed, and compared to conventional methods of composition quantification from APT data.

2. Computational Details

2.1. APT Data Simulation

In order to exemplify the method proposed in the present paper, two different types of composition distributions frequent in semiconductor materials have been simulated. One of them is the phase separation that occurs during the epitaxial growth of some semiconductor compounds, where lattice misfit induced strain leads to compositional instabilities. This phenomenon is common in semiconductors such as InGaAs grown on InP [31], InGaAs grown on GaAs [32] or InGaN grown on sapphire [33]. The characterization of the composition at atomic-scale of the resulting material is essential to understand both the growth process and the optoelectronic properties of the material. In the following, the simulation of this phenomenon will be called “model 1”. The second simulation (“model 2”) is related to the abrupt changes of composition that are desired in many semiconductors devices. For example, layers of defined dimensions with specific compositions such as QWs are often needed to allow designs related to the band engineering, where the quantization of the energy of the electrons requires that the interfaces between the layers are as sharp as possible. Some examples of semiconductor designs including layers are InGaAs layers between InAlAs layers for spintronics [34], GaAs layers between AlGaAs layers for purifiers [35] and InAs layers between GaAs layers for resonant Bragg systems [36]. The characterization of the composition through the interfaces allows the detection of deviations with regards to the designed heterostructure due to phenomena such as segregation.

For model 1, i. e., gradual variations of composition, the $In_xGa_{1-x}As$ alloy has been chosen because phase separation occurs frequently in the epitaxial growth of this material [37–39]. A composition distribution consisting of a sinusoidal variation in In from 5% In to 15% In with a wavelength of 10 nm along the Z axis has been considered. With regards to model 2 (simulation of an abrupt variation of composition), a QW heterostructure consisting of an InAs QW located between GaAs barriers has been chosen, as it is a very common design [36,40,41]. Two three-dimensional supercells of these materials of 10x10x10 and 15x15x15 nm^3, respectively, have been built. In order to simulate APT data from these materials, the crystalline atomic positions of the supercells have been randomly displaced a distance ranging from −0.2 to +0.2 nm, and 40% of the atoms have been removed randomly to achieve the average efficiency of the current commercial atom probe instruments that vary from approximately 37% to 80% [42]. In the $In_xGa_{1-x}As$ alloy, a simplification has been introduced as no changes of the lattice parameter due to the variations of the composition are included. This is because a change in 5% of the In content varies the lattice parameter only in a 0.35% (using Vegard's law). In the case of the QW, the strain due to the lattice mismatch between the layers has been introduced using a finite element analysis package.

Fig. 1 shows the simulated APT data of model 1 and 2 described above, where In, Ga and As atoms are shown as red, blue and black dots, respectively. Fig. 1a) represents a cross-section of the entire volume of the $In_xGa_{1-x}As$ alloy. As it can be observed, the movement of the atoms from their true crystal sites and the absence of 40% of the atoms produce a loss of the crystal order. There is an increase in In atoms in the region z = 0 to z = 50 with regards to the region z = 50 to z = 100, although the variation in the number of red dots is not easy to be detected visually because of its small magnitude. Fig. 1b) represents a cross-section of the simulated InAs/GaAs QW structure where the three layers are well distinguishable, although the crystalline order of the semiconductor is again lost.

2.2. Conventional Methods of Analysis of APT Data

For comparison purposes, we have also applied conventional methods for composition quantification in APT to the simulated data explained above. These methods are the voxelization and the proximity histograms profiles [17]. The main parameters used in these methods are detailed below.

2.2.1. Voxelization

This method consists of dividing the data into voxels with constant