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Theoretical and experimental factors affecting measurements of semiconductor mean inner potentials

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Abstract. We use density functional theory to explore the effect on calculations of semiconductor mean inner potentials of the presence of reconstructions, changes in lattice spacing and adsorbates on the surfaces of parallel-sided thin specimens. We also use electron holography to illustrate several factors that affect experimental measurements of mean inner potentials of semiconductor nanowires.

1. Introduction

Quantitative electron holography of semiconductors is of interest for measuring dopant distributions, specimen thickness profiles, compositions, and charge densities at interfaces and surfaces. For many applications, the mean inner potential V_0 of the semiconductor should be known accurately. However, measurements of V_0 are sensitive to many factors, including specimen charging, bonding, dynamical diffraction and the nature of the specimen surface [1]. In addition, the specimen orientation and thickness must be known accurately. Here, we assess some of the factors that affect predictions and measurements of V_0 by performing calculations of potentials in semiconductors with adsorbates and surface reconstructions and by using electron holography to record phase images of GaAs nanowires.

2. Calculation details and results

V_0 was calculated for selected semiconductors using the projector-augmented wavefunction approach within the density functional theory (DFT) formalism, implemented as GPAW [2]. The calculation volume contained the material of interest and a region with no material, as shown in Fig. 1 and also used by Kruse et al. [3]. The Hartree potential V_H was determined from the valence electrons, screened core electrons and nuclei for region B marked in Fig. 1 relative to that in region A. As will be detailed elsewhere, in order to take into account the unscreened core charges, a second potential V_{EC} was calculated by solving Poisson's equation for the unscreened charge according to the expression [2]

$$\rho(\mathbf{r}) = \tilde{\rho}(\mathbf{r}) + \sum_a \Delta\rho^a(\mathbf{r} - \mathbf{R}^a),$$

after which $V_0 = V_H + V_{EC}$.

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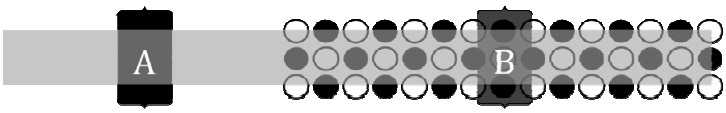

Fig. 1. Calculation geometry used in this work, with the material of interest and a region of vacuum.

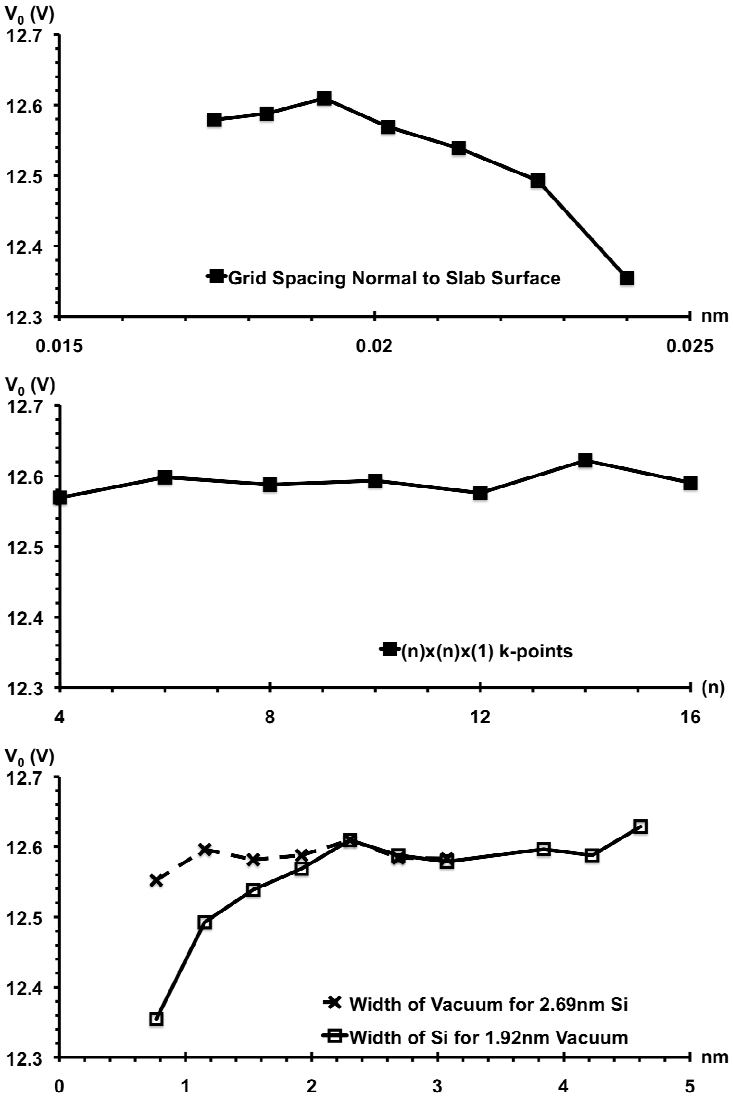

Fig. 2. Verification of parameter stability for calculations of V_0 for parallel-sided Si specimens with (110) surfaces. Grid spacings of $h_x = 0.0226$ nm and $h_y = 0.0192$ nm were used in the [001] and [1-10] directions parallel to the surface of the slab.

The sensitivity of V_0 to a range of input parameters is shown in Fig. 2 for parallel-sided Si specimens with (110) surfaces. As specimens containing only a few monolayers of material have decreased values of V_0, 2.69 nm of Si and 1.92 nm of vacuum were typically used in subsequent calculations for (110) surfaces. It was found that, in order to ensure stability, the atomic lattice of the crystal should be located on grid points in the direction normal to the surface of the slab. Unless otherwise stated, the calculation parameters used were $8 \times 8 \times 1$ k-points, 0.0192 nm per real-space grid point in the direction normal to the surface of the slab, and the PBE exchange-correlation functional [4], parallelized over 8 processor cores using domain decomposition.

2.1. Surface orientation and reconstruction

Table 1 shows the results of calculations of V_0 for parallel-sided Si slabs with different crystallographic orientations, with atom positions that are unchanged from those in a bulk Si crystal, and with the parameters optimized for each simulation. The difference between the calculated values for (110), (111) and (211) surfaces is below 0.05 V. However, the value for a (100) surface is 0.32 V above that for a (110) surface. Most significantly, the introduction of a (2×1) reconstruction on the (100) surface, with atom positions included from Ref. [5], changes V_0 by almost 0.6 V when compared to the unreconstructed (100) surface.

2.2. Adsorbates

Table 2 shows the results of calculations of V_0 for parallel-sided Si slabs with (110) surface orientations that have one atomic layer of either Si, C or Ge on their surfaces, both with the surface atoms located at positions that Si atoms would occupy on a perfect bulk Si lattice and then with the positions of either all of the atoms in the calculation (for a Si surface) or just the surface atoms (for C and Ge surfaces) relaxed until the force on the atoms was below 0.5 eV / nm. Although the arrangements of atoms in the surface layer may not reflect the positions of adsorbed atoms that would occur experimentally, the calculations illustrate the sensitivity of V_0 to the identities and positions of atoms in the surface layers, with a single relaxed adsorbed layer of C changing the calculated value of V_0 by more than 0.5 V.

2.3. Different semiconductors

Table 3 shows a comparison of DFT calculations of V_0 for different semiconductors with values that would be obtained from neutral atom electron scattering factors [6]. The fact that the present DFT values are close to those in Ref. [3] (also reproduced in Table 3) provides confidence in the applicability of the GPAW simulator for calculations of V_0 for a wide range of materials.

Table 1. V_0 for Si calculated as a function of surface orientation for optimized parameters.

Silicon surface	V_0 (V)
(110)	12.59
(111)	12.63
(211)	12.64
(100)	12.91
(100) (2×1) from [5].	12.32

Table 2. V_0 for Si calculated as a function of surface composition and relaxation.

Surface	V_0 (V)
Si (all-relaxed)	12.52
Si(C)	14.12
Si (C-relaxed)	12.01
Si (Ge)	12.46
Si (Ge-relaxed)	12.53

Table 3. V_0 calculated for different semiconductors with (110) surfaces using the present density functional theory (DFT) calculations, compared with values reproduced from the DFT calculations of Ref. [3] and obtained using neutral atom electron scattering factors (V_{fel}) taken from Ref. [6].

Material	V_0 (V) $_{DFT}$	V_0 (V) $_{Ref.\ [3]}$	V_0 (V) $_{fel}$
Si	12.59	12.57	13.76
Ge	14.69	14.67	15.60
AlP	11.40	11.39	13.42
AlAs	12.29	12.34	13.97
GaP	13.57	13.63	14.60
GaAs	14.15	14.19	15.38
InP	13.85	13.90	15.22
InAs	14.13	14.34	15.47
CdS	13.02	-	13.87

3. Electron holography results

Semiconductor nanowires are, in many ways, ideally suited for experimental measurements of V_0 as their orientations and cross-sections can be determined accurately and minimal specimen preparation is required. Fig. 3 shows part of a representative electron hologram of a GaAs nanowire that has a diameter of 160 nm, acquired at 300 kV using an FEI Titan 80-300 TEM operated in Lorentz mode. The figure also shows experimental phase profiles acquired from a wire oriented at the [110] zone axis and rotated about its long axis to several orientations. The phase profiles illustrate four of the difficulties of measuring V_0 experimentally, even from nanowires: the sensitivity of the line profiles to crystallographic orientation as a result of both changes in projected thickness and dynamical contributions to the phase shift, the difficulty of removing phase wraps at the edges of the wire where the sample thickness changes rapidly, the possibility of charging of the wire as a result of secondary electron emission during electron irradiation, resulting in a ramp in vacuum outside the wire for the 19.1° phase profile, and the unknown state of the nanowire surface.

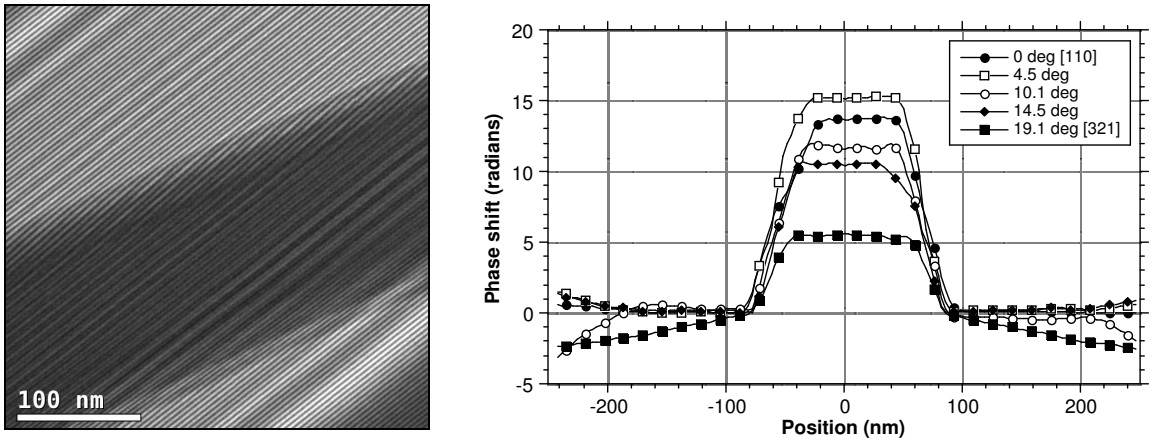

Fig. 3. Electron hologram and phase profiles for a GaAs nanowire examined at different orientations.

4. Conclusions

We have obtained preliminary density functional theory simulations and experimental measurements that illustrate several of the factors that may affect measurements of semiconductor mean inner potentials. The calculations illustrate the sensitivity of the mean inner potential to the presence of adsorbed or reconstructed layers on the specimen surface. The electron holography results illustrate several additional practical complications associated with experimental measurements of mean inner potentials, even for the relatively simple GaAs nanowire system.

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