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Growing multiple layers of porous semiconductors
—A molecular-dynamics study

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Abstract – The deposition of Si/Ge multilayers was simulated using classical molecular-dynamics simulations. The layers consisted of 40 Ge or Si clusters of 1018 atoms deposited at 1 eV/atom on a porous Ge layer previously deposited onto a Si bulk lattice. These multilayers were numerically analyzed, and simulated transmission electron microscope images of the layers were formed. The results showed that the porous Ge layers were capable of supporting the deposition without collapsing, thus forming multiple superimposed layers with different characteristics. The image simulations suggest that identification of elements within the new layers is possible through contrast analysis.

Porous silicon surfaces and silicon nanocrystals have been shown to exhibit strong visible photoluminescence (PL) at room temperature, contrary to bulk material [1]. The PL of porous or nanocrystalline germanium and Si/Ge has also been shown to reveal a similar effect [2,3]. Although anodization or chemical etching are the most common methods used to manufacture porous layers, low-energy cluster beam deposition (LECBD) can also be used for the same purpose [4–6]. Results using the top-down methods have shown that the PL wavelength is shifted as a function of the porosity of the layer due to the change in size of the layer’s nanoparticles, a trait not shared with LECBD using clusters of constant mean size.

In addition to comprehensive experimental results, a great number of numerical simulations of LECBD have also been performed (e.g., [7,8]). These simulations have shown that the porosities of the deposited layers depend strongly on the deposition energy ranging from thermal energies to about 1 eV per atom: with the lower energies, the clusters land softly on the substrate, leaving considerable room between themselves, resulting in a high porosity; and with the higher energies, the clusters are flattened upon landing, decreasing the amount of empty space and resulting in little to no porosity. Thus, with LECBD, the PL wavelength only shifts when the clusters start to lose integrity as the layer’s porosity approaches zero.

Through anodic etching of wafers, it has been demonstrated that it is also possible to produce multiple superimposed layers of different porosities [9–11]. Due to differences in refractive index caused by differing porosities, the superposition of alternating high- and low-porosity layers results in optically isolated layers that allow waveguiding to occur [12]. While top-down methods can effectively only be used to obtain layers of the same element, using LECBD for this purpose gives rise to the new possibility of switching between sputtering targets during deposition to obtain multielemental multilayers, allowing further tailoring of the layer’s optical properties.

The purpose of this study is to investigate the formation of porous semiconductor multilayers through cluster deposition as simulated using classical molecular dynamics (MD) [13]. As a first step, the deposition of Ge clusters onto a Si substrate has already been simulated at different energies to find a relationship between deposition energy and layer porosity [8]. This work continues with the simulation of further deposition of Si and Ge clusters on these porous layers.

Prior to the deposition simulations, a cluster of 1018 Si atoms and a cluster of 1018 Ge atoms (each about 3.3 nm in diameter, a suitable mean value for an experimental size distribution) were relaxed using multiple thermal annealing processes and then thermalized to 77 K, corresponding to the experimental setup of our laboratory, where the condensation chamber can be cooled with
liquid nitrogen. After this, simulations of 40 consecutive cluster depositions at 1 eV/atom were run for both Si and Ge clusters separately. This is the highest deposition energy used in our previous work, and it is of the same order of magnitude as the corresponding velocity measured experimentally for neutral clusters of this size [5]. Two different deposition targets were used in these simulations: a porous layer containing 50 Ge clusters deposited on a Si substrate at 10 meV/atom, and one deposited at 100 meV/atom. More details on these targets can be found in reference [8] (referred to in that article as the “main simulations”). For the Si clusters, another set of simulations was run at a deposition angle of 45 degrees.

The atomic interactions were modeled using Tersoff potentials for Si and Ge [14]. The temperature of the simulation cells was controlled at the bottom 3 Å (corresponding to three atomic layers) of the substrates using the Berendsen temperature control algorithm [15] with a time constant of 250 fs. The bottom layer of atoms in each cell was fixed, to simulate the effect of a bulk substrate. The time for each deposition was 1 ns, which corresponded to the complete relaxation of the system after deposition. For increased statistics, each of the six runs was performed four times with different randomization parameters.

A visual inspection of the atomic cross-sections of the deposited layers shown in fig. 1 reveals that the original porous structure can provide enough support for the deposition of energetic clusters without collapsing. However, since nothing can stop the clusters from entering the surface pores, the upper region of the original layer becomes engulfed within a newly formed layer. This effectively forms a multilayer consisting of the Si bulk, the porous Ge layer, and the new layer; the thicknesses of the last two depend on the amount of clusters deposited in each phase. It is apparent from the depth profiles of these multilayers (shown in fig. 2) that the density of the new top layers approaches that of the bulk. A greater amount of simulated cluster depositions would result in a thicker layer with this density, hiding beneath it the original porous layer. Likewise, more clusters deposited during the low-energy phase would give a thicker porous layer. After this, the whole process can be repeated to produce a number of alternating porous and dense layers.

When the clusters deposited at high energy consist of the same element as the porous layer (in this case, Ge), there is no ex post facto way to distinguish between “old” and “new” atoms in the new layer without tracking them throughout the simulation process. However, when the elements differ, the border region becomes a mixture consisting of nanocrystalline regions of both elements. The thickness of this region is about 10 nm, as can be seen in fig. 2(b). Depositing at an angle of 45° reduces this thickness by about 20%, as illustrated in fig. 2(c); however, a comparison of the graphs in fig. 2 also shows that the new Si layer deposited at 45° is slightly porous, i.e. its density is less than that of the bulk. This is because the deposited clusters press down on the structure with only half of the deposition energy, reducing the flattening effect of the collision — the pore morphology is more elastic in the horizontal direction since the support structure of the layer is mostly vertical. The relative density of the layers deposited at 45° approaches that of the layers deposited at 500 meV/atom on bulk in our previous work, implying that a deposition energy closer to 2 eV/atom would be needed to achieve bulk density when depositing at 45°.

In addition to being analyzed numerically, the deposited layers were used further to produce simulated cross-sectional transmission electron microscope (TEM) images. The simulations were performed with the multislice technique [16] using the program EMS [17], in which the sample is divided into thin slices before the wave function of the electron beam is calculated as it propagates through each slice in turn. The individual slice thickness used in these simulations was 2.0 Å, and there were a total of 65 slices in the whole sample. Other simulation parameters included a beam energy of 200 kV, an objective aperture of 2.0 nm⁻¹, a spherical aberration of 1.0 mm and no defocus. The sampling was 1024 × 1024.

The sample simulated images shown in fig. 3 reveal that the Ge deposition images display a visible amount of more contrast between cluster atoms (dark) and void (light) in the mixed layer as compared to either kind of Si deposition images: the top third of fig. 3(a) is darker than the top thirds of the other two images, while the bottom two-thirds of each image are nearly identical.
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Fig. 2: Depth profiles of multilayers with (a) 40 deposited Ge clusters, (b) 40 deposited Si clusters, and (c) 40 Si clusters deposited at an angle of 45°, on original porous layers of 50 Ge clusters deposited on a Si substrate. The solid curves show the original porous layer profiles with black being the 10 meV deposited layer and grey the 100 meV deposited layer. The horizontal dotted lines show the bulk densities for silicon (higher) and germanium (lower). The remaining dotted and dashed curves show the total densities of the new multilayers from all runs. The peak at the top of the bulk is due to Si dimers formed through surface relaxation [18].

Fig. 3: Simulated TEM images of (a) a 40-cluster Ge layer and (b) a 40-cluster Si layer deposited straight-on, and (c) a 40-cluster Si layer deposited at an angle of 45°, on porous Ge. The dark mass at the bottom indicates the Si bulk and the light line above it the Si surface dimer peak.

Furthermore, Si layers deposited at 45° display even less top-layer contrast than Si layers deposited straight-on, even though one cluster on the right side of the images is slightly darker in fig. 3(c). This is because it was subject to more pressure from the bombarding clusters in that particular deposition, which also explains why it is situated slightly lower than in the other images. Thus, it may be possible to distinguish between layer elements using contrast comparison. While the difference between straight-on and 45° Si depositions is due to the lower density of the latter layer, density effects cannot explain the difference between the Ge and Si layers, since Si has a higher density. Unfortunately, quantitative contrast analysis was not possible because the total contrast was dominated by the dimer-bulk coupling (seen at the bottom of each image).

As this work demonstrates, the deposition process itself does not damage the porous layers. However, real-time diffusion effects may greatly alter the structure of the newly deposited multilayers in ways that remove any advantages that these novel structures may have. Unfortunately, simulating diffusion in the size and time scales of molecular dynamics is not directly possible. If these possibly adverse effects can be avoided, these multilayer structures may have a variety of different applications. Besides the aforementioned waveguiding, porous layers of materials other than semiconductors may also be considered for use in molecular storage; for instance, porous multilayer grids of metals may be used to store hydrogen.

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