# Crystallization of the Si-$SiO_2$ superlattices stimulated by a uniaxial periodic potential

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A new type of superlattice based on thin Si and $SiO_2$ layers has been obtained. The application of a uniaxial periodic potential and thermal annealing cause the superlattices to crystallize, forming a new hexagonal crystal structure.

The semiconductor superlattices obtained by means of molecular-beam epitaxy or deposition from organometallic compounds have unique electronic and optical properties and several of their parameters are better than those of the known semiconductors.[1] Because of the slight difference in the lattice constants of the semiconductors comprising the superlattice, its crystal structure is essentially the same as that of bulk semiconductors. We have attempted to determine whether a completely new crystal structure of the superlattice can be obtained by means of a deliberately produced uniaxial periodic potential.

To change the crystal structure of the superlattice, the potential wells which appear as a result of alternating two materials with different widths of the energy gap $E_g$ must be rather deep: on the order of the binding energy. As the starting materials we have therefore used Si and $SiO_2$, in which the difference in $E_g$ is $\sim 7$ eV. Since the surface energy associated with the interface must be of the same order of magnitude as the bulk energy of the system, we made each Si and $SiO_2$ layer 1.0 nm thick. To insure that the only periodic potential in such a superlattice will be a deliberately produced uniaxial periodic potential, we used amorphous Si and $SiO_2$ layers. Under these conditions a deliberately produced potential apparently will be primarily responsible for the formation of the crystal and electronic systems of the superlattice.

The layered structure was prepared by rf sputtering of Si and $SiO_2$ alternately on the targets in a spectrally pure argon at a pressure $P = 1.2 \times 10^{-3}$ Torr. The chamber was pumped beforehand to $P = 10^{-7}$ Torr. The deposition rate of silicon was 0.09 nm/s and that of $SiO_2$ was 0.04 nm/s. The temperature of the substrate during sputtering was no greater than 70 °C. As substrates we used a polished single-crystalline KÉF-4.5 silicon with a (100) or (111) orientation and with a surface roughness no greater than 0.3 nm. To avoid the influence of the substrate's crystallinity on the superlattice, we deposited on it beforehand a 0.1-$\mu$m-thick layer of amorphous nickel. The superlattice consists of eighty-one layers, whose first and last layer are $SiO_2$. By means of diffraction of fast electrons by reflection from the structure (RHEED) we showed that the structural period of the superlattice was held within 0.2 nm. The thickness of the Si and $SiO_2$ layers was therefore $1.0 \pm 0.1$ nm.

Using a profile Auger spectroscopy, we showed that the superlattices which we obtained are indeed layered materials without any other impurity elements of concen-

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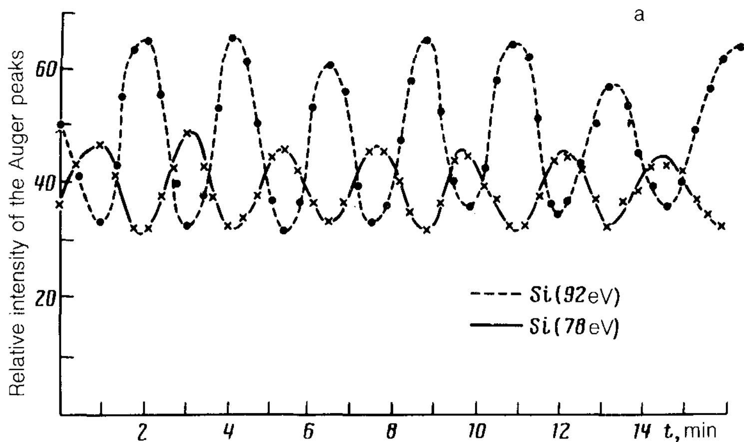


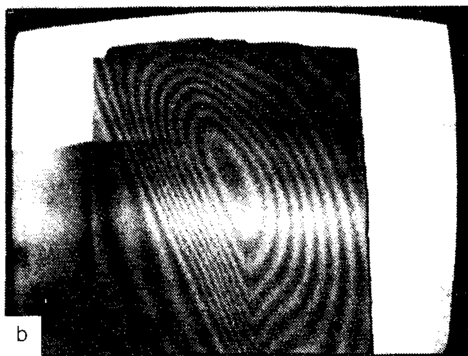


FIG. 1.

tration greater than $10^{10}$ cm$^{-3}$. Figure 1a is a plot of the intensity of the Auger signals of Si (92 eV) and $SiO_2$ (78 eV) as a function of the etching time of the structure. Figure 1b shows a crater formed as a result of etching of the superlattice by argon ions directed at a glancing angle; the black and white ovals are the secondary-electron images of the Si and $SiO_2$ layers. These figures show that this structure is a layered materials with a periodic alternation of the Si and $SiO_2$ layers.

The crystal structure of the superlattice was studied using a JEM-6A transmission electron microscope. We expected that as a result of application of a uniaxial periodic potential, the superlattice would acquire a new crystal structure with a preferred symmetry axis. The electron-diffraction measurements showed, however, that the superlattice is amorphous, as indicated by the diffuse halo in the electron-diffraction patterns (Fig. 2a). This circumstance forced us to anneal the structures in argon atmosphere at $P = 10^{-3}$ Torr. Annealing the superlattice for 0.5 h at temperatures $T = 300$–$400$ °C led to the appearance of a polycrystalline phase: the electron-diffrac-

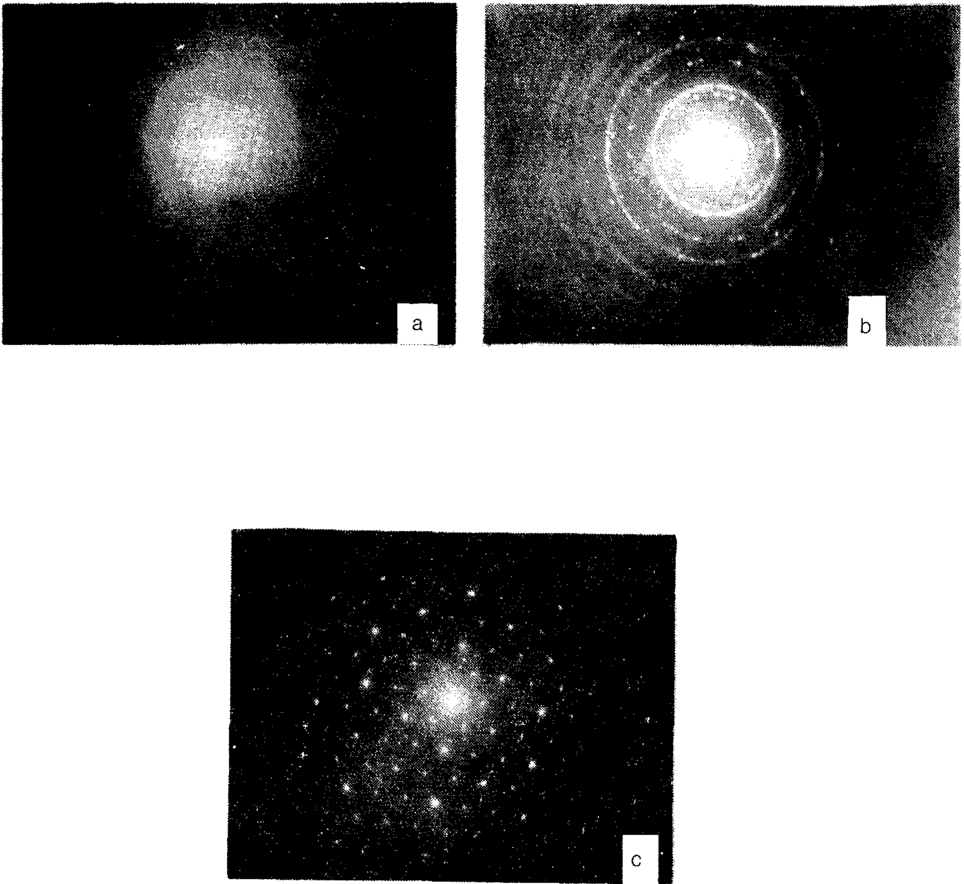


FIG. 2.

tion patterns revealed the presence of thin rings and many weak reflections (Fig. 2b). Annealing for two minutes at $T = 700$ °C led to the appearance in the electron-diffraction patterns of point reflections characteristic of a hexagonal crystal structure (Fig. 2c). These electron-diffraction patterns had no reflections from crystalline Si and $SiO_2$. In other words, the crystal structure of the superlatttice, with its large interplanar spacing, $d = 0.479$ nm, is entirely different from the crystal structures of Si and $SiO_2$ (the maximum interplanar spacing for Si is $d = 0.313$ nm and for $SiO_2$ it is $d = 0.425$ nm). Upon annealing the superlattice thus crystallized to a new hexagonal crystal structure with the lattice constants $a = 0.553$ nm and $c = 0.90$ nm. There are seven known pressure-induced modifications of Si: of which four are hexagonal modifications of Si and three are hexagonal modifications of $SiO_2$ (Ref. 3). The lattice constants of this superlattice, however, do not match any of these modifications. A bombardment of Si metal atoms with energies of 1–10 eV causes the surface layer (0.1 $\mu$m) of Si to change.[4] One of the crystal modifications of Si changed by bombardment

is very similar to the hexagonal structure of the superlattice (its interplanar spacing is $d = 0.479$ nm). It can be assumed that the application of a periodic uniaxial potential and thermal annealing cause the cubic Si to undergo a transition to a hexagonal Si and cause the $SiO_2$ lattice to transform to a new structure with parameters of the hexagonal Si. It should be pointed out that the layers of the superlattice are not blurred as a result of annealing; the profile Auger analysis confirmed that the layers alternate periodically. Furthermore, the modulation depth of the intensity of the Auger signals increased by 10% due to the etching of the superlattice. This increase can be attributed to the change in the density of matter in the layers.

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