$Si/Si_{1-x}Ge_x$ epitaxial layers and superlattices. Growth and structural characteristics

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(Submitted April 3, 1996; accepted for publication December 25, 1996)
Fiz. Tekh. Poluprovodn. **31**, 922–925 (August 1997)

Si, Ge, and $Si_{1-x}Ge_x$ epitaxial layers and $Si/Si_{1-x}Ge_x$ superlattices have been obtained on (100) and (111) silicon substrates by molecular-beam epitaxy. The growth processes and the structural characteristics and chemical composition of the structures were studied by x-ray diffraction and Auger spectroscopy. It is shown that under the experimental conditions for obtaining $Si/Si_{1-x}Ge_x$ superlattices structurally perfect, strained superlattices with satellites up to ± 5 orders can be obtained. © *1997 American Institute of Physics.* [S1063-7826(97)00708-4]

Modern epitaxial methods for growing semiconductor layers make it possible to monitor growth processes at the atomic level. Structures (heterojunctions, quantum wells, superlattices) with controllable characteristics for micro- and optoelectronics can be produced by combining different types of semiconductors and epitaxial layers of different thickness. The most thoroughly studied structures to date are those based on group-III and group-V semiconductors, the most important of which crystallize in the zinc blende structure. In some cases, lattice-matched components can be chosen for the structures; this makes it possible to achieve controlled heteroepitaxy and to obtain high-quality structures. However, the most important structures for applications are still structures based on elementary semiconductors, especially Si — the principal material of semiconductor electronics.

The properties of bulk $Si_{1-x}Ge_x$ crystals have been investigated for many years (see, for example, Ref. 1). Depending on the chemical composition, the band gap in these compounds can range from 1.1 to 0.7 eV and, for example, $Si_{1-x}Ge_x$-based photodetectors can operate in the spectral range 0.5–1.8 μm, so that they can be used in fiber-optic communication lines. However, the large lattice mismatch ($\Delta a = 4.2\%$ at $T = 300$ K) in the case where $Si_{1-x}Ge_x$ layers are grown in silicon substrates results in a high mismatch-dislocation density at the interface.

Progress in the development and investigation of strained quantum-well structures and heterostructures based on silicon (see, for example, Refs. 2 and 3) promises development of fundamentally new devices for micro- and optoelectronics in the system $Si/Si_{1-x}Ge_x$.[4,5]

In the present study we investigated the structural characteristics of Si, Ge, and $Si_{1-x}Ge_x$ layers and superlattices in the $Si/Si_{1-x}Ge_x$ system, prepared by molecular beam epitaxy (MBE) on (100) and (111) silicon substrates.

One of the main problems in growing perfect quantum-well structures and heterostructures based on Si and Ge is to assure layerwise two-dimensional stepped growth at relatively low epitaxy temperatures ($T \leqslant 550$ °C) while avoiding three-dimensional growth with a high germanium content in the layers, since otherwise the surface morphology of the $Si_{1-x}Ge_x$ layers is disrupted and a high defect density arises in them.

In the heteroepitaxy of lattice-mismatched semiconductors, there exist critical thicknesses of epitaxial layers up to which the lattice mismatch is compensated for by stresses in the layers. In the case at hand, this results in a tetragonal distortion of the unit cell. The typical values of the critical thicknesses for $Si_{1-x}Ge_x$ layers on substrates with growth temperatures $T \simeq 500$ °C are 1000 Å for layers with $\Delta a = 1\%$ ($\sim 20\%$ Ge) and only 10 Å for $\Delta a = 4.2\%$ (pure germanium). When the critical thicknesses are exceeded, relaxation of mechanical stresses occurs in the layers and mismatch dislocations are formed.

Epitaxial layers of Si and $Si_{1-x}Ge_x$ were grown on (100) and (111) substrates by molecular-beam epitaxy in a Katun' system with substrate temperatures $T = 400 - 830$ °C in vacuum with a residual pressure not exceeding 5×10^{-8} Pa. A high-energy electron diffractometer built into the growth chamber made it possible to monitor within 3 Å the thickness of the layers being grown and the degree of their structural perfection according to the rearrangements of the structure of the growth surface directly during the growth process.

The pre-epitaxial preparation of the silicon substrates consisted in chemical etching away of the natural oxide and depositing a $\sim$1-μm-thick passivating oxide film with the aim of later removing the film in a controllable manner in the growth chamber. During the heating of the silicon substrates in the growth chamber up to a temperature $T \simeq 850$ °C with residual vapor pressure $\leqslant 10^{-7}$ Pa, the interaction of the weak Si vapor flow ($F_{Si} \simeq 10^{15}$ cm^2/s) with the surface of the substrates according to the reaction

$$SiO_2 + Si \rightarrow SiO\uparrow \quad (1)$$

produced in a time of 2–5 min an oxygen-free, atomically clean surface and resulted in the appearance of clear reflections of 7×7 and 2×1 structures for (111) and (100) orientations, respectively.

The minimum temperature at which epitaxial growth of the Si buffer layers could be achieved was equal to

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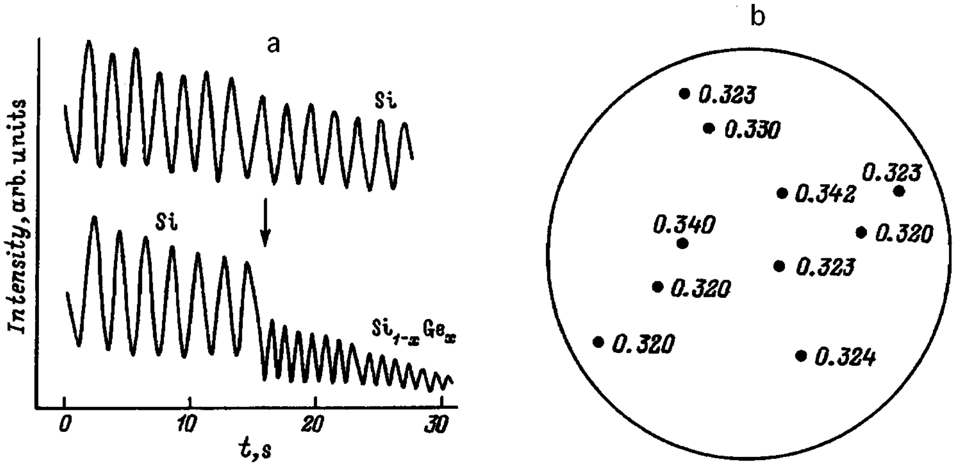

FIG. 1. a — Oscillations of the central HEED reflection at time t during growth of Si epitaxial films (top) and the change occurring in the oscillations when the Ge source (bottom, arrow) for growing $Si_{1-x}Ge_x$ epitaxial layers is switched on b — distribution of the chemical composition in the plane of a $Si_{1-x}Ge_x$ epitaxial layer with thickness $d \simeq 1$ μm, obtained by molecular-beam epitaxy on a Si (100) plate. The values of x are indicated.

$\sim$400 °C with a growth rate of $1.0-1.5$ Å/s. The oscillations of the central HEED reflection (see Fig. 1a), according to which the epitaxial growth rate was determined, remained distinct and stable, indicating that the growth of the epitaxial layers was a two-dimensional process.

The conditions for obtaining epitaxial Ge and $Si_{1-x}Ge_x$ layers on Si (111) substrates were investigated. Specifically, the optimal growth parameters of epitaxial germanium films on silicon substrates with surface restructurings $(7\times7)\rightarrow(5\times5)\rightarrow(2\times8)\rightarrow(1\times1)$ were determined and studied in the temperature range $T=350-650$ °C. The epitaxial $Si_{1-x}Ge_x$ layers ranged in thickness from 50 Å to 1 μm and in Ge content $x\simeq0.07-0.70$. The growth conditions made it possible to obtain $Si_{1-x}Ge_x$ epitaxial layers on Si substrates, 60–76 mm in diameter, with a relative composition uniformity of $\pm1\%$.

Figure 1b shows the distribution of the Ge content in $Si_{1-x}Ge_x$ epitaxial layers for the regimes prescribed for obtaining layers with $x\simeq0.35$. It is obvious that the uniformity of the Ge distribution is relatively high, and that the composition matches well the prescribed growth conditions. Figure 2 shows diffraction-reflection curves for $Si/Si_{1-x}Ge_x$ heterosystems with different chemical compositions of the epitaxial layers.

The composition of the $Si_{1-x}Ge_x$ epitaxial layers was monitored according to the angular separation $\Delta\theta$ between the positions of the peaks in the x-ray diffraction reflection pattern assuming that Vegard's law holds [Vegard's law holds well in $Si_{1-x}Ge_x$ (the lattice constants are $a=5.431$ Å for Si and $a=5.657$ Å for Ge at $T=300$ K)], taking into account the corrections for the degree of relaxation of the strained layers. The error in measuring $\Delta\theta$ is $\pm1''$ (irrespective of the composition). This makes it possible to determine the composition of the layers with an absolute accuracy of $\pm0.3\%$. The elastic stresses existing in heterojunctions affect the determination of the chemical composition of the layers. However, as a result of the relatively large radii of curvature of the silicon plates with epitaxial layers, in determining the composition of the layers the corrections made so as to take into account the relaxation of the mechanical stresses in the heterostructure are small.

The intensity of the diffraction reflection peaks from the thin Si, Ge, and $Si_{1-x}Ge_x$ epitaxial layers and from the $Si/Si_{1-x}Ge_x$ superlattices is a fraction of a percent of the intensity of the reflection peak from the silicon substrate. However, these peaks are still intense enough to determine the thickness of the epitaxial layers with a relative accuracy of $\pm3\%$.

The profiles of the chemical composition distribution in the heterostructures and $Si/Si_{1-x}Ge_x$ superlattices were also investigated by layerwise analysis in a 09 IOS-005 Auger spectrometer. The surface of the samples was etched with argon ions at a constant rate in the energy range 2.0–3.5 keV and with ion-beam current densities 180–350 $\mu A/cm^2$ and ion-beam diameter $\sim$0.75 μm. The intensity (number N of electrons) of the Ge Auger peak (energy $E=1146.8$ eV) was measured continuously. The typical dependence of the change in the intensity of the Ge Auger peak over the depth of the sample (the accumulation time t_a with a constant etch rate is proportional to the distance from the sample surface) is shown in Fig. 3. As one can see from Fig. 3, the periodicity and thickness of the separate Si and $Si_{1-x}Ge_x$ layers (70-Å SiGe and 90-Å Si) hold up quite well. The Ge molar

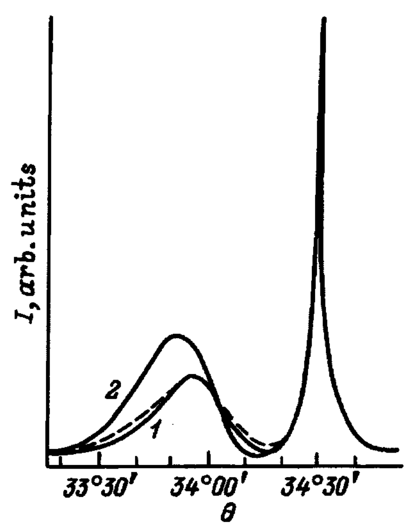

FIG. 2. Diffraction reflection curves for $Si_{1-x}Ge_x$ heterostructures on Si (100) substrates. x: *1* — 0.39, *2* — 0.44. The intensity I scale is logarithmic.

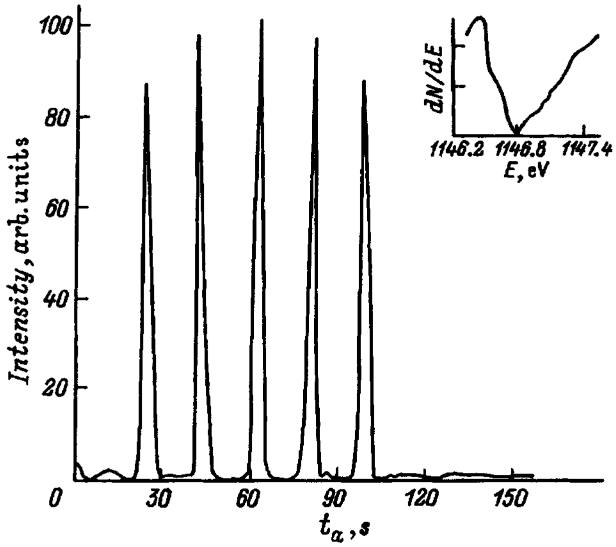

FIG. 3. Variation in the intensity of the Ge Auger peak $E=1146.8$ eV with layerwise etching of the surface of a strained $Si_{1-x}Ge_x$ superlattice by Ar ions. The ion energy is 2.8 keV, the current is $250 \mu A/cm^2$, and the ion beam diameter is 0.75 μm. The period of the superlattice is 160 Å. Inset: Ge Auger peak.

fraction in the $Si_{1-x}Ge_x$ layers, determined according to the ratio of the Ge and Si Auger peak intensities for heterostructures and $Si/Si_{1-x}Ge_x$ superlattices, correspond satisfactorily to the prescribed regimes of experimental growth of the structures.

The structural characteristics of the Si and $Si_{1-x}Ge_x$ buffer layers, as well as the periodic $Si_{1-x}Ge_x$ structures with period $d=100-300$ Å were investigated by the x-ray diffraction method in a DRON-3 diffractometer with a double-crystal scheme in the $(n,-n)$ geometry with a Si (100), (111) monochromator and a Cu$K\alpha 1$ radiation line ($\lambda=1.54051$ Å). The x-ray diffraction method makes it possible to determine at the same time the stress distribution, the chemical composition, and the period of the superlattices. The mechanical stresses arising as a result of the lattice mismatch between the buffer layer and the substrate and between the buffer layer and the superlattice results in bending of the silicon plates; this bending can be determined according to the change in the angular position of the main diffraction peak. The average curvature of the silicon plates with the $Si_{1-y}Ge_y$ ($y \simeq 0.5x$) buffer layers was equal $R^{-1} \simeq 0.2$ m^{-1}.

The period d of the $Si_{1-x}Ge_x$ superlattices was determined according to the angular separation $\Delta(2\theta)$ between the satellites in the x-ray diffraction spectra

$$d=\frac{\lambda}{\Delta(2\theta)} \cos \theta_s^{-1}, \qquad (2)$$

where θ_s is the Bragg angle of reflection from the substrate.

During the growth of $Si_{1-x}Ge_x$ superlattices the condition for pseudomorphic growth of the epitaxial layers was satisfied (strained superlattices), and satellites up to ± 5 orders were observed in the x-ray diffraction reflection spectra. The presence of numerous, regularly spaced, and well-defined x-ray satellites attests to the structural perfection of the superlattices[6] — the existence of sharp boundaries between the layers, uniformity of their chemical composition, etc.

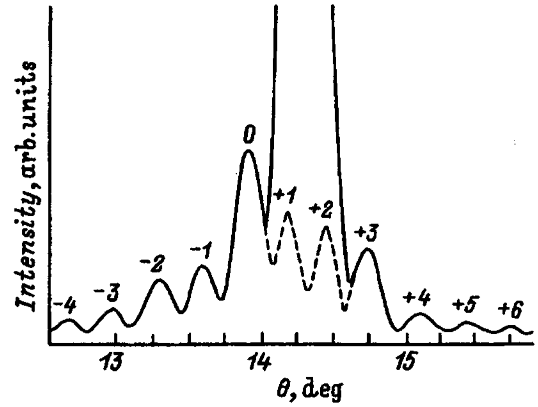

FIG. 4. X-Ray diffraction intensity versus diffraction angle for a five-period $Si_{1-x}Ge_x$ superlattice on a Si (111) substrate with a 0.2-μm-thick Si buffer layer. Measurement conditions: CuKα1 radiation line with wavelength $\lambda=1.54051$ Å, Si (100) monochromator, (400) reflection. Superlattice parameters: period 181 Å, SiGe layer thickness 72 Å, Si layer thickness 109 Å. The peaks of the negative $(-i)$ and positive $(+j)$ satellites for the superlattice are numbered. The dashed line represents the oscillations of the x-ray diffraction of the satellites which are masked by the intense diffraction reflection peak from the silicon substrate.

The typical x-ray diffraction pattern of a five-period $Si_{1-x}Ge_x$ superlattice ($x \simeq 0.35$, period $d \simeq 181$ Å, SiGe layer thickness 72 Å, Si thickness 109 Å) on a silicon (111) substrate with a 0.2-μm-thick Si buffer layer is shown in Fig. 4. The main (wide at the base) peak at $\theta=14° 13'$ is due to the (111) reflection from the silicon substrate and is a reference reflection in the present case. The intensity of the diffraction reflection peaks from the $Si/Si_{1-x}Ge_x$ superlattice equals fractions of a percent of the intensity of the reflection peak from the silicon substrate. Several relatively wide but well-separated negative $(-i)$ and positive $(+j)$ satellites, which attest to the good uniformity of the layers over thickness, can be seen in Fig. 4.

The free-carrier density in the Si, Ge, and $Si_{1-x}Ge_x$ epitaxial layers was equal to $10^{15}-10^{17}$ cm^{-3}. To control the electrical characteristics of the layers of the superlattices, the Si layers were doped with boron with a resulting density of $10^{17}-10^{19}$ cm^{-3}.

In summary, our investigations of the growth of Si, Ge, and $Si_{1-x}Ge_x$ layers and our study of their structural characteristics have shown that structurally perfect heterostructures and $Si/Si_{1-x}Ge_x$ superlattices with a large area and prescribed chemical composition can be obtained.

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Translated by M. E. Alferieff