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Microscopic symmetry properties of (001) Si/Ge monolayer superlattices

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Short-period Si/Ge superlattices have special symmetry properties due to the tetrahedral bonding. In [001]-oriented $(\mathrm{Si})_m/(\mathrm{Ge})_n$ superlattices (m monolayers Si, n monolayers Ge) the primitive unit cell is determined by a multiple of two monolayers. Thus, for $m+n$ odd the periodicity is doubled to $2(m+n)$ monolayers. Low-temperature molecular-beam epitaxy is used to realize atomically sharp Si/Ge superlattices. The symmetry properties have been studied by selected area diffraction with the transmission electron microscope and by Raman spectroscopy. Clear evidence is observed for the 10-monolayer periodicity in a $(\mathrm{Si})_2/(\mathrm{Ge})_3$ superlattice.

Superlattices (SL's) composed of atomically thin layers of Si and Ge are artificial semiconductors with tailorable basic properties. The thickness of the individual layers, the periodicity, and the built-in strain distribution are strongly related to the band structure.[1] Therefore, the electronic and optical properties of such structures are of considerable physical[2,3] and technological[4] interest. In order to realize high-quality short-period Si/Ge SL's it is necessary to modify the growth conditions in molecular-beam epitaxy (MBE). The samples have been prepared at very low growth temperatures in the range 280–350 °C on [001]-oriented Si and Ge substrates. The substrate temperature has been modulated during deposition of the individual Si and Ge layers to achieve sharp interfaces with optimized lateral uniformity.[5,6]

In this Rapid Communication we mainly concentrate on the symmetry aspects of $(\mathrm{Si})_m/(\mathrm{Ge})_n$ SL's. After a description of the structural properties of some $(\mathrm{Si})_m/(\mathrm{Ge})_n$ SL's and the growth method we report on experimental studies using selected area diffraction (SAD) with the transmission electron microscope (TEM), and Raman spectroscopy.

The lateral strain and the superlattice period d_{SL} in the growth direction reduces the symmetry with respect to the diamond structure of the host materials. Depending on the composition of the SL there are tetragonal (m and/or n odd) and orthorhombic crystal structures (m,n even).[7] These symmetry properties arise from the tetrahedral arrangement in the diamond lattice. The direction of the bonds switches from [110] to the 90°-rotated $[1\bar{1}0]$ orientation within (001) lattice planes going from one atomic layer to the next. As a consequence the vertical extension of the primitive unit cell can only be a multiple of two monolayers (ML). Therefore, in the case of $m+n$ even, the periodicity is $d_{\mathrm{SL}}=(m+n)$ ML, whereas for $m+n$ odd it is doubled to $d_{\mathrm{SL}}=2(m+n)$ ML. The extreme case of a perfectly ordered and free-standing $(\mathrm{Si})_1/(\mathrm{Ge})_1$ SL in the [001] direction represents a SiGe zinc-blende crystal. There are six different space groups[7] for $(\mathrm{Si})_m/(\mathrm{Ge})_n$ SL's on (001) substrates. In the case of (001) $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ SL's only two different space groups (D_{2d}^5, D_{2d}^9) are possible.[8] This is a consequence of the zinc-blende structure which represents the host lattice for III-V materials. Therefore, periodicity doubling for $m+n$ odd and orthorhombic structures for m,n even are peculiar for group-IV-element SL's.

Figure 1 shows the primitive unit cells and the corresponding Brillouin zones of three $(\mathrm{Si})_m/(\mathrm{Ge})_n$ SL's. For $(\mathrm{Si})_2/(\mathrm{Ge})_2$ the unit cell contains two Si and two Ge atoms. The atomic arrangement demonstrates that all Si atoms as well as all Ge atoms are located exclusively on (110) lattice planes defined by the unit vectors $\mathbf{a}_2$ and $\mathbf{a}_3$. Therefore, an ideal $(\mathrm{Si})_2/(\mathrm{Ge})_2$ SL in the [001] direction corresponds to a $(\mathrm{Si})_1/(\mathrm{Ge})_1$ SL in the [110] direction. For m,n even all the interfacial Si-Ge bonds lie within the lattice plane defined by $\mathbf{a}_1$ and $\mathbf{a}_3$. As a consequence the symmetry is not tetragonal but orthorhombic. There is only a twofold rotational symmetry parallel to the [001] growth direction. The orthorhombic structure in this case causes a reduction of the symmetry-induced fourfold-degenerate L conduction-band minima into twofold-degenerate states along the [110] and $[1\bar{1}0]$ directions. Therefore, an optical anisotropy perpendicular to the [001] axis is expected for SL's with m,n even.[9] The orthorhombic symmetry is also reflected in the lattice-

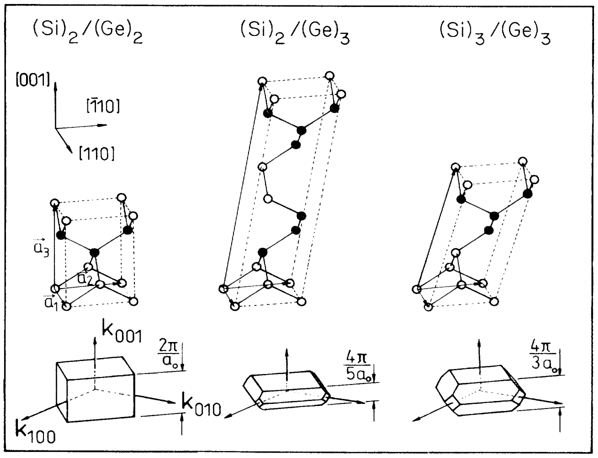

FIG. 1. Schematic diagram of the primitive unit cells for several $(\mathrm{Si})_m/(\mathrm{Ge})_n$ SL's in the [001] direction. The corresponding Brillouin zones are plotted below. The open and solid symbols represent the Si and Ge atomic positions, respectively.

dynamical properties.[7] Experimental observation of the orthorhombic symmetry in SL's with m,n even [for example, in $(\mathrm{Si})_2/(\mathrm{Ge})_2$] will be very difficult because of atomic steps on the surface of the substrate and at the Si/Ge interfaces. Each monatomic step causes a 90° rotation of the orthorhombic cell. Since the mean terrace width for the best samples on Ge substrates is on the order of 100 Å as measured by *in situ* low-energy electron diffraction (LEED),[6] there will be several 90°-rotated domains within the area of the probing-laser spot. In addition, Fig. 1 shows the primitive unit cells of $(\mathrm{Si})_2/(\mathrm{Ge})_3$ and $(\mathrm{Si})_3/(\mathrm{Ge})_3$. The first Brillouin zone is schematically drawn for each SL. For $(\mathrm{Si})_2/(\mathrm{Ge})_3$ the compositional periodicity is 5 ML. Consequently the microscopic unit cell is doubled to $d_{\mathrm{SL}}=10$ ML. There are four Si atoms and six Ge atoms within the primitive unit cell in this case. $(\mathrm{Si})_3/(\mathrm{Ge})_3$ provides a vertical periodicity of 6 ML and therefore contains only six atoms within the primitive unit cell. Owing to the translational symmetry of these SL's the vertical extension of the Brillouin zone is smaller for $(\mathrm{Si})_2/(\mathrm{Ge})_3$. In both cases, $m+n$ odd and m,n odd, a fourfold symmetry axis exists which is parallel to the [001] direction. For example, $(\mathrm{Si})_3/(\mathrm{Ge})_3$ has a fourfold inversion-rotational symmetry [S_4: rotation around [001] by 90° followed by a reflection on a (001) plane[10]]. That means the [110] and [1$\bar{1}$0] directions perpendicular to the growth direction are equivalent and the structure is tetragonal.

The SL's $(\mathrm{Si})_2/(\mathrm{Ge})_3$ and $(\mathrm{Si})_4/(\mathrm{Ge})_6$ differ in their atomic arrangement within the unit cell and in their symmetry properties. $(\mathrm{Si})_2/(\mathrm{Ge})_3$ provides a centered tetragonal structure with space group D_{4h}^{19} ($I4_1/amd$), whereas the structure of $(\mathrm{Si})_4/(\mathrm{Ge})_6$ is a centered orthorhombic structure and belongs to the space group D_{2d}^{9} ($I4m2$). However, there is no difference between these SL's as far as the vertical translational symmetry is concerned: it is in both cases 10 ML. The size and the shape of the unit cell and the Brillouin zone are very similar.

From the previous discussion of the microscopic symmetry properties it is obvious that the expected effects are only observable when atomically sharp interfaces are achieved. We have performed detailed studies using *in situ* methods like LEED and Auger electron spectroscopy in order to determine the optimum growth conditions. Details about the preparation technique have been published elsewhere.[5,6] In the following we present results of SAD and Raman investigations of the samples with the sharpest interfaces achieved so far.

Figure 2(a) shows a SAD pattern of a $(\mathrm{Si})_4/(\mathrm{Ge})_6$ SL in a [110] projection. The four additional spots between the indexed main spots parallel to the growth direction (vertical axis) indicate the 10-ML periodicity. The diffraction pattern represents a section through a (110) plane of the reciprocal lattice. It is a superposition of diffraction patterns originating from the SL and the substrate. Detailed investigations of the structural properties which can be extracted from SAD patterns as well as cross-sectional TEM micrographs of short-period Si/Ge SL's have been presented.[5,11] In Fig. 2(b) [SAD pattern of $(\mathrm{Si})_2/(\mathrm{Ge})_3$], SL spots reflecting the artificial ordering are clearly observable. It should be mentioned at this point that the thickness of 2-ML Si plus 3-ML Ge is only about 7 Å. The separation of the SL diffraction spots is exactly the same as for $(\mathrm{Si})_4/(\mathrm{Ge})_6$ (period length about 14 Å) as pointed out by the arrows. This demonstrates the 10-ML periodicity in the growth direction for $(\mathrm{Si})_2/(\mathrm{Ge})_3$. The intensity of the SL spots for $(\mathrm{Si})_2/(\mathrm{Ge})_3$ and $(\mathrm{Si})_4/(\mathrm{Ge})_6$ is different and reflects the different arrangement of the Si atoms and Ge atoms within the unit cell. For $(\mathrm{Si})_2/(\mathrm{Ge})_3$ the SL spots in the middle are more intensive than the spots closest to the main spots. The intensity distribution is reversed for $(\mathrm{Si})_4/(\mathrm{Ge})_6$ where the SL spots in the middle (between the main spots) are lowest in intensity. However, the fact that the 10-ML periodicity is observed in SAD for $(\mathrm{Si})_2/(\mathrm{Ge})_3$ does not mean that the Si/Ge interfaces have no monatomic steps within the whole area of the probing electron beam. It is primarily a consequence of the tetrahedral bonding of the host lattice (diamond structure).

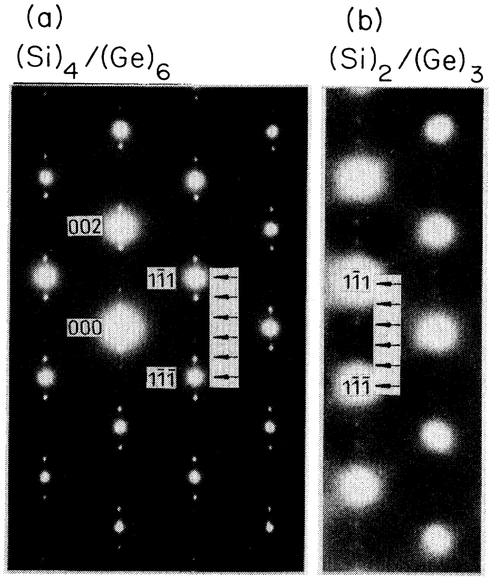

FIG. 2. Selected area diffraction pattern with the electron beam aligned along the [110] direction: (a) 140-period $(\mathrm{Si})_4/(\mathrm{Ge})_6$ SL on a Ge(001) substrate. (b) 100-period $(\mathrm{Si})_2/(\mathrm{Ge})_3$ SL on a Si(001) substrate. The vertical axis is parallel to the [001] growth direction. The arrows mark the positions of the diffraction spots for a SL providing 10-ML periodicity.

Another method to analyze short-period SL's in detail is Raman spectroscopy. We have studied a series of SL's with a minimum of two atomic planes in one layer, namely $(\mathrm{Si})_2/(\mathrm{Ge})_3$, $(\mathrm{Si})_3/(\mathrm{Ge})_3$, $(\mathrm{Si})_2/(\mathrm{Ge})_5$, and $(\mathrm{Si})_3/(\mathrm{Ge})_5$. For these samples we expect a periodicity of 10, 6, 14, and 8 ML, respectively. All measurements have been performed in near-backscattering geometry: 001(110, 110)00$\bar{1}$. Mainly longitudinal modes are observed in this configuration due to Raman selection rules. Figure 3 shows the Raman spectra of the SL's and a $\mathrm{Si}_{0.4}\mathrm{Ge}_{0.6}$ alloy. The alloy was prepared by annealing the $(\mathrm{Si})_2/(\mathrm{Ge})_3$ SL under high-vacuum conditions at 780 °C for 200 min. This procedure is well known to cause sufficient interdiffusion so that a random alloy is achieved.[12] In

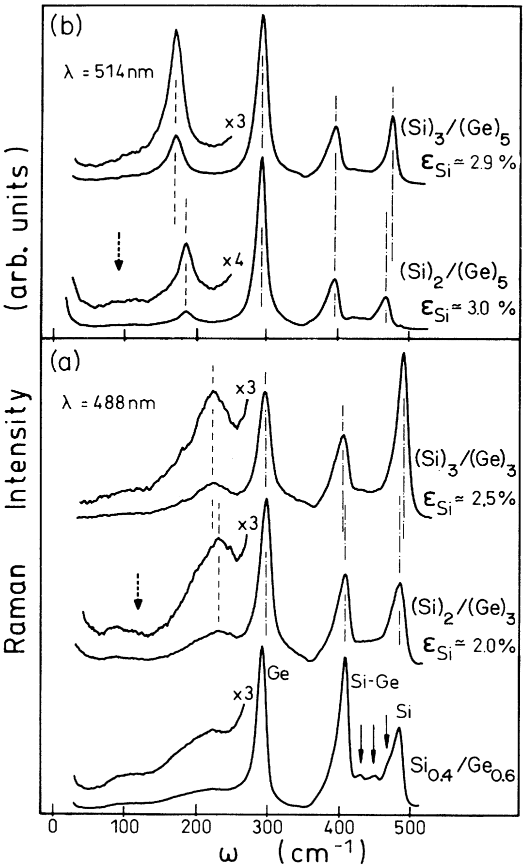

FIG. 3. Raman spectra of (a) a $(Si)_3/(Ge)_3$ and a $(Si)_2/(Ge)_3$ SL with 100 periods, and a $Si_{0.4}Ge_{0.6}$ alloy; (b) a $(Si)_2/(Ge)_5$ and a $(Si)_3/(Ge)_5$ SL containing 180 periods on a Ge substrate. The samples in (a) are grown on special strain-adjusting buffer layers (Ref. 5) on a Si substrate. The built-in lateral strain of the Si layers ϵ_{Si} is given for each SL. The measurements were performed at room temperature.

Si_xGe_{1-x} alloys there are basically three optical modes related to Ge-Ge, Si-Ge, and Si-Si vibrations. Due to the statistical distribution of the Si and Ge atoms there are weak, additional Raman peaks[13] marked by the arrows in the lowest spectrum plotted in Fig. 3(a). There are several significant differences between the Raman spectra of the SL's and the $Si_{0.4}Ge_{0.6}$ alloy. For the SL's in Fig. 3(a) additional (folded acoustic) modes appear between 200 and 250 cm^{-1} (dashed vertical lines) and the intensity of the Si-Ge-alloy mode is considerably smaller than for the alloy. Another remarkable feature is that the weak Raman peaks of the alloy between the Si-Ge and the Si modes do not appear for the SL's. Owing to the 10-ML periodicity for $(Si)_2/(Ge)_3$, an additional folded acoustic branch giving rise to a doublet mode (between zero and the mode marked by the dashed line) is expected. The dashed arrow in the spectrum of the $(Si)_2/(Ge)_3$ SL indicates the calculated frequency (117 cm^{-1}) of the Raman allowed mode.[14] Since there is only a weak and relatively broad shoulder in this spectrum, and because there is also some structure at this energy range in the spectrum of the corresponding alloy, one cannot definitely conclude from the Raman spectra that the 10-ML periodicity for $(Si)_2/(Ge)_3$ exists. On the other hand it is not expected that there is a substantial intensity for this mode due to the structure-factor argument. In the microscopic lattice model we expect 10 longitudinal phonons for $(Si)_2/(Ge)_3$. A simple consideration based on the Si and Ge bulk phonon dispersion combined with Brillouin-zone folding can be used to analyze the features of the spectra.[15–17] In the Fourier analysis of the vertical concentration profile for $(Si)_2/(Ge)_3$ the first-order-folded doublet mode vanishes. Comparison of the Raman spectra of $(Si)_2/(Ge)_3$ and the alloy reflects the limitation of the interface sharpness which is achieved in this system. However, there are still clear differences in the phonon spectra of SL's as compared to the alloy. In the spectrum of the $(Si)_3/(Ge)_3$ SL the folded acoustic mode is shifted to lower energies as compared to $(Si)_2/(Ge)_3$. In addition, the Si-Ge vibration is reduced in intensity, indicating that there are less Si-Ge bonds in this sample. The shift of the Si mode is due to the different thickness of the Si layers.

In Fig. 3(b) the series of short-period SL's is continued with $(Si)_2/(Ge)_5$ and $(Si)_3/(Ge)_5$. Both samples are grown on [001]-oriented Ge substrates. The energy of the first-order-folded acoustic doublet mode $m = \pm 1$ for $(Si)_3/(Ge)_5$ is in very good agreement with the frequency of 171 cm^{-1} calculated from the elastic continuum model.[17] For $(Si)_2/(Ge)_5$ the expected frequency of the related doublet mode is 186 cm^{-1}. The variation of the individual Si-layer thickness from 3 to 2 ML is again reflected in the shift of the Si mode.[16] In the microscopic model we expect not 7 ML but a 14-ML vertical periodicity for $(Si)_2/(Ge)_5$, giving rise to an additional doublet mode close to the energy marked by the dashed arrow. As for $(Si)_2/(Ge)_3$, there is a weak structure at about 100 cm^{-1}. The different intensity ratios for the Si, Si-Ge, and Ge modes for the SL's in Figs. 3(a) and 3(b) is due to the different compositions and also to the fact that different laser lines have been used for excitation.

In conclusion, we have shown by means of SAD that the symmetry of $(Si)_2/(Ge)_3$ is not given by the compositional periodicity of 5 ML but is determined by the microscopic arrangement of the atoms within the new unit cell leading to a 10-ML periodicity in the growth direction. Raman spectra of various extremely short-period $(Si)_m/(Ge)_n$ SL's demonstrate the ordered structure in comparison to an $Si_{0.4}Ge_{0.6}$ alloy. Changes of individual layer thicknesses of one atomic plane are clearly observable. With low-temperature MBE it is possible to realize extremely short-period Si/Ge SL's down to a 4-ML periodicity.

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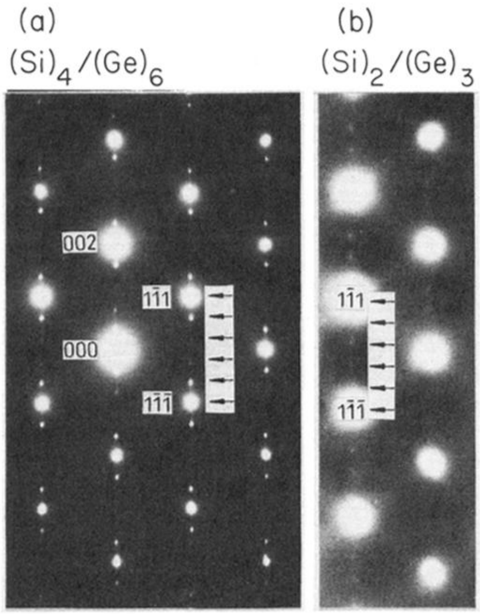

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