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A One-Dimensional SiGe Superlattice Grown by UHV Epitaxy

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Abstract. One-dimensional SiGe superlattices with periods ranging from 100 to 800 Å have been deposited on Si substrates by periodically varying the Ge content of a mixed $Si_{1-x}Ge_x$ multilayer structure from $x=0$ to $x=0.15$. The deposition was successful, employing an UHV evaporation technique at a substrate temperature of 750° C fulfilling the four conditions: Single crystal growth, no interdiffusion, two-dimensional growth, and pseudomorphic growth. It is shown that mismatch above $8 \cdot 10^{-3}$ favours growth by three-dimensional nucleation. The experimentally determined spacing of misfit dislocations is compared with theoretical results obtained by van der Merwe. The pseudomorphic growth behaviour of layers thinner than a critical thickness could be confirmed.

Index Headings: One-dimensional superlattice – Misfit dislocations – Nucleation of films – UHV epitaxy

We consider a one-dimensional SiGe superlattice with alternating $Si_{1-x}Ge_x$ and Si layers on a Si substrate. It has been shown [1] that such a one-dimensional superlattice consisting of a multilayer structure yields a novel class of man-made semiconductors. If the period of the superlattice is shorter than the electron mean free path one expects mini-zones in the momentum space, yielding narrow allowed and forbidden bands. Some interesting electrical and optical properties of the semiconductor superlattice were calculated [1–3]. Attempts were made to grow superlattice structures consisting of III–V compounds [1, 4–6]. The most promising III–V superlattice consists of GaAs and AlAs because of the low lattice mismatch between these two III–V compounds ($1.4 \cdot 10^{-3}$). For this structure also experimental results concerning the electrical and optical effects have been reported [7–9]. We want to investigate the SiGe superlattice on a Si substrate because elemental semiconductors are very well known, the use of a Si substrate makes this superlattice compatible with the common Si technology and new optical effects are predicted [2]. The SiGe superlattice exhibits the great disadvantage of a considerable mismatch between the components Si and Ge ($4 \cdot 10^{-2}$, thirty times larger than the mismatch between GaAs and AlAs). On the other hand, solving the problem of considerable mismatch allows the use of a much wider variety of superlattice components. The growth of a multilayer structure with considerable mismatch and extremely thin layers (≈ 100 Å) is not self-evident. The conditions to be fulfilled by epitaxy are listed and discussed in Section 1. The experimental apparatus and the experimental results are described in Sections 2 and 3, respectively. The interest is concentrated to good quality epitaxy at relatively low temperatures, to misfit dislocations, and to the first stages of heteroepitaxial growth. Most problems could be investigated within single layers of Si and $Si_{1-x}Ge_x$ on Si (Subsections 3.1 and 3.2). The results about misfit dislocations in multilayer structures are summarized in Subsection 3.3.

1. Conditions of Superlattice Epitaxy

In order to realize the SiGe superlattice, problems have to be solved which are connected with heteroepitaxy of Ge and Si and growth of very thin layers. The epitaxy

of the superlattice must fulfil the following four requirements:
(a) Single crystal growth.
(b) No interdiffusion.
(c) Two-dimensional growth.
(d) Pseudomorphic growth.
These requirements are discussed in more detail in the following section.

(a) Single Crystal Growth. The growth mode (single crystalline, polycrystalline, amorphous) is strongly dependent on the deposition method and deposition temperature. Aharoni *et al.* [10] reported temperatures between 1100 and 1250° C for the chemical vapour deposition of single crystal $Si_{1-x}Ge_x$ layers onto Si substrates. On the other hand, Jona [11] and Thomas *et al.* [12] reported temperatures as low as 300° C for the homoepitaxial deposition of Si under UHV conditions. Ito *et al.* [13] deposited single crystal Ge films on Si substrats by UHV evaporation technique at temperatures above 330° C. The UHV evaporation technique is a deposition method permitting the single-crystal growth of Si and Ge at low temperatures.

(b) No Interdiffusion. A low deposition temperature is necessary in order to avoid the interdiffusion of Si and Ge leading to a smear out of the periodic potential. This is achieved if the diffusion length is much less than the thickness d of one layer of the superlattice:

$$\text{diffusion length } (Dt)^{1/2} \ll d \tag{1}$$

(t: time, D: diffusion coefficient).

The diffusion coefficient is

$$D = D_0 \cdot \exp(-E/kT). \tag{2}$$

After McVay *et al.* [14] the values of D_0 and E (Ge in Si) are $1535\,\text{cm}^2/\text{s}$ and 4.7 eV, respectively. With $(Dt)^{1/2} = 10^{-7}$ cm and $t = 10^4$ s the condition for the upper limit of the deposition temperature T is determined.

$$T \leqq 1100\,\text{K} \; (\approx 830^\circ\,\text{C}). \tag{3}$$

Therefore, our preparation is performed by UHV evaporation technique at temperatures below 830° C.

(c) Two-Dimensional Growth. The epitaxial growth occurs either by the motion of monatomic steps on the surface [15] (two-dimensional growth) or by nucleation of three-dimensional nuclei, island growth and coalescence of the islands. Only the two-dimensional growth by the motion of steps yields smooth thin layers. Growth by three-dimensional nucleation is unsuitable for the realization of the superlattice. On a clean Si surface homoepitaxial growth proceeds by the motion of steps (two-dimensional growth). However, even faint traces of contaminants especially carbon disturb the motion of steps and three-dimensional island growth occurs [16, 17]. After Joyce *et al.* [18] the amount of carbon required to change the growth mode may represent 0.01 of a monolayer. To overcome this difficulties a careful pretreatment of the Si substrate and a clean environment (e.g. UHV) are necessary. In the literature two kinds of pretreatment are described. Joyce *et al.* [18] and Cullis *et al.* [16] have preheated the substrate at 1250° C in the UHV apparatus. At this temperature silicon oxide volatilizes very fast and carbon is removed from the surface presumably by solid state diffusion. Abbink *et al.* [19] have achieved two-dimensional growth by UHV evaporation on a freshly deposited surface grown after a 900° C anneal of the substrate. Up to now only three-dimensional nucleation and island growth was observed with Ge films on Si substrate despite careful pretreatment [13, 16, 20]. Obviously the mismatch between Si and Ge favours three-dimensional growth. Therefore we did not deposit a superlattice with alternating Si and Ge layers, but with alternating Si and $Si_{1-x}Ge_x$ layers. It is one aim of our investigation to determine the upper limit of Ge concentration (of the $Si_{1-x}Ge_x$ layer) permitting two-dimensional growth.

(d) Pseudomorphic Growth. The mismatch η between film and substrate is usually accomodated by a network of misfit dislocations lying in the interface and by elastic strain ε of the film. A row of parallel misfit dislocations (edge dislocations, slip vector b lying in the interface) with spacing p accomodates b/p of the mismatch.

$$\eta = 2(a_1 - a_2)/(a_1 + a_2) = b/p + |\varepsilon| \tag{4}$$

(a_1, a_2: lattice constant of film and substrate, respectively). The ratio of accomodation by elastic strain to that by misfit dislocations depends mainly on mismatch, material strength, layer thickness, original dislocation configuration, and heat treatment. Van der Merwe [21] has considered the thermodynamic equilibrium situation of misfit dislocations. In his equilibrium theory dislocation spacing depends only on mismatch, material strength and layer thickness. In Fig. 1 the calculated dislocation spacing p ($Si_{1-x}Ge_x$ film on Si substrate) is plotted against film thickness assuming equal shear modulus for substrate, film and interface and a $1/2\langle 110\rangle$ slip vector. The calculations

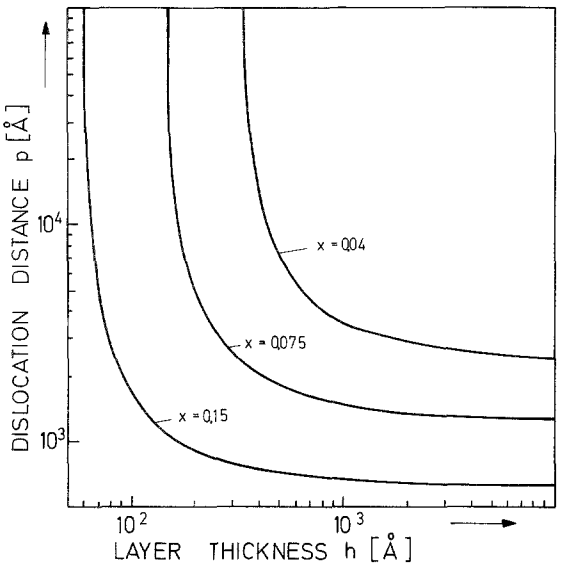

Fig. 1. Dislocation distance p versus thickness h of $Si_{1-x}Ge_x$ layers on Si substrate calculated according to (5), after the theory of van der Merwe

have been performed with (4) and the approximate equation for the elastic strain (5) given by [21].

$$\varepsilon = \frac{(1-2\sigma)(2-\eta)(1+\eta)\cdot b}{2(1-\sigma)^2(2+\eta)^3 h} \ln[2\beta(1+\beta^2)^{1/2} - 2\beta^2] \quad (5)$$

$$\beta = 4\pi\eta/(1-\sigma)(2+\eta)^2$$

(σ: Poisson's number, h: film thickness, b: length of slip vector, η: mismatch).

The original term for ε has been slightly modified to take into account the diamond structure of Si and Ge. Instead of the lattice constant [21] we take the length of slip vector because the strain field of dislocations depends on the latter quantity. (In the primitive cubic cell considered by [21] lattice constant and length of slip vector are equal.) The main result of the van der Merwe theory is, that the ratio between elastic strain and accomodation by misfit dislocations is strongly influenced by film thickness. In very thin films there are no misfit dislocations (Fig. 1, $p \to \infty$). This first stage of growth is called pseudomorphic growth. Above the critical thickness h_c, generation of misfit dislocations begins.

If the accomodation of mismatch is made by dislocations with a spacing p within each interface, the dislocation density N_v in a one-dimensional superlattice on (100) substrate is given by

$$N_v = 2/pd \quad (6)$$

(e.g. with a layer thickness $d = 50$ Å, with $Si_{0.85}Ge_{0.15}$ and Si as alternating layers the dislocation density assuming accomodation by misfit dislocations is as high as $6 \cdot 4 \cdot 10^{11}/cm^2$). Therefore, we have to require pseudomorphic growth for a good quality material. Up to now no theory exists about misfit dislocations in a superlattice using van der Merwe's conception. However, Matthews *et al.* [22] estimate the critical thickness of a superlattice layer to be four times higher than the critical thickness of a single layer. We investigated experimentally the dislocation structure of superlattices consisting of layers smaller than the critical thickness.

2. Experimental Procedure

Deposition was carried out in a bakeable UHV evaporation chamber evacuated by a turbomolecular pump and a titanium sublimation pump achieving a base pressure of $5 \cdot 10^{-11}$ Torr. The chamber contained a Si and a Ge source, both provided with shutters. Si was evaporated by means of an electron gun, Ge from a heated Al_2O_3 crucible. The substrate was indirectly heated by a graphite heater. The temperature of the substrate surface was measured with a thermocouple. The substrate materials were single crystalline, dislocation free and one side polished (001) Si wafers with 3.8 cm diameter and a thickness of 300 µm. After chemical cleaning, 3 µm were removed from the polished side by sputtering. Before deposition, the substrates were thermally cleaned within the chamber by heat treatment for 10 min at 900° C [19], and the temperature was then reduced to the required growth temperature. The growth rate was 4 Å s^{-1} monitored by a calibrated quartz crystal. During the epitaxial process the pressure in the chamber raised to typically $1 \cdot 10^{-8}$ Torr. The epitaxial films obtained were investigated by optical microscopy, transmission electron microscopy and x-ray topography.

3. Results

As mentioned above, a certain set of conditions was demanded for growing superlattice structures. At first, Si films were grown on Si substrates at various substrate temperatures for examining the defect density and the temperature range of single-crystal growth of the Si films. Then $Si_{1-x}Ge_x$ films were grown on Si substrates at various substrate temperatures, with different Ge content and various film thicknesses. These

experiments should proof whether the conditions 1 to 4 can be fulfilled. Using the results of these preliminary experiments, SiGe superlattice structures were prepared and investigated.

3.1 Si *Homoepitaxy*

Si films of 1 μm thickness were grown on Si substrates at substrate temperatures in the range from 550 to 800° C. Single crystal films were obtained with low defect density in agreement with the results of Jona [11] and Thomas *et al.* [12].

3.2 $Si_{1-x}Ge_x$ *Heteroepitaxy*

Basically, a Si film of 0.3 μm thickness was deposited on the substrate before the heteroepitaxy or the superlattice epitaxy began in order to realize a fresh surface. $Si_{0.85}Ge_{0.15}$ films of 1 μm thickness were grown at temperatures in the range from 650 to 800° C. The films revealed single crystal growth at all substrate temperatures. Because of the lattice mismatch a square grid pattern of straight misfit dislocations running in ⟨110⟩ directions was observed in the interface between substrate and film. However, $Si_{1-x}Ge_x$ films grown at

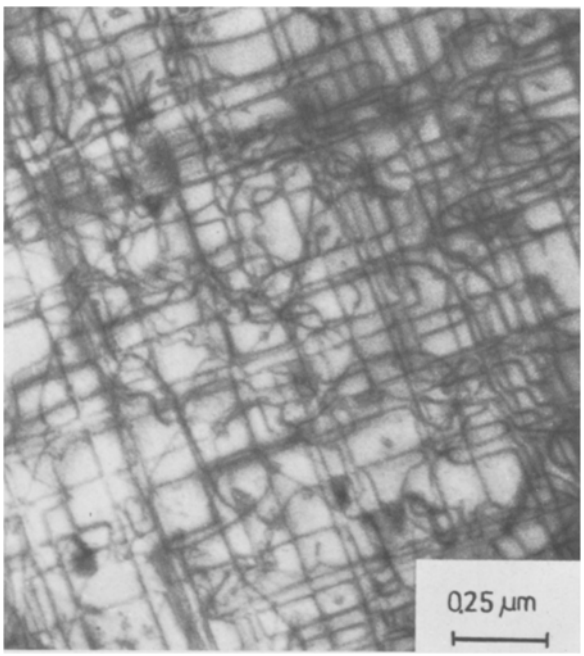

Fig. 2. Dislocation array of a $Si_{0.85}Ge_{0.15}$ layer of 1 μm thickness grown at 700° C (TEM micrograph)

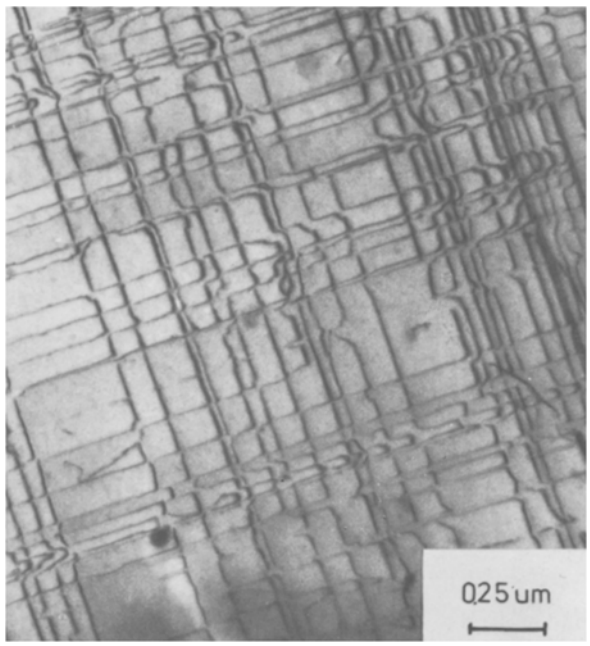

Fig. 3. Net of misfit dislocations of a $Si_{0.85}Ge_{0.15}$ layer of 1 μm thickness grown at 750° C (TEM micrograph)

650° C contained an inhomogeneous Ge distribution and a high density of dislocations within the layer. $Si_{1-x}Ge_x$ films grown at a substrate temperature of 700° C had a homogeneous Ge distribution. In addition to a net of misfit dislocations a great number of threading dislocations running through the layer was observed as shown in Fig. 2.

At a substrate temperature of 750° C almost no threading dislocations but only a net of misfit dislocations lying in the interface between substrate and film were observed. The layer itself exhibits a low defect density. Figure 3 shows the TEM micrograph of such a $Si_{0.85}Ge_{0.15}$ film grown at 750° C.

It has been shown that the defect density within the deposited films decreases with increasing epitaxy temperature. On the other hand, condition 2 requires a substrate temperature lower than 830° C. Therefore, we decided to use a substrate temperature of 750° C for the subsequent epitaxial processes. If the Ge content amounted $x \geqq 0.2$, the $Si_{1-x}Ge_x$ layers exhibited three-dimensional growth. Figure 4 shows the TEM micrograph of a $Si_{0.75}Ge_{0.25}$ layer 200 Å thick. The layer consists of three-dimensional growth centres forming an island-like pattern. With increasing layer thickness the growth centres coalesce to larger islands, as shown in Fig. 5. The islands contain dislocation

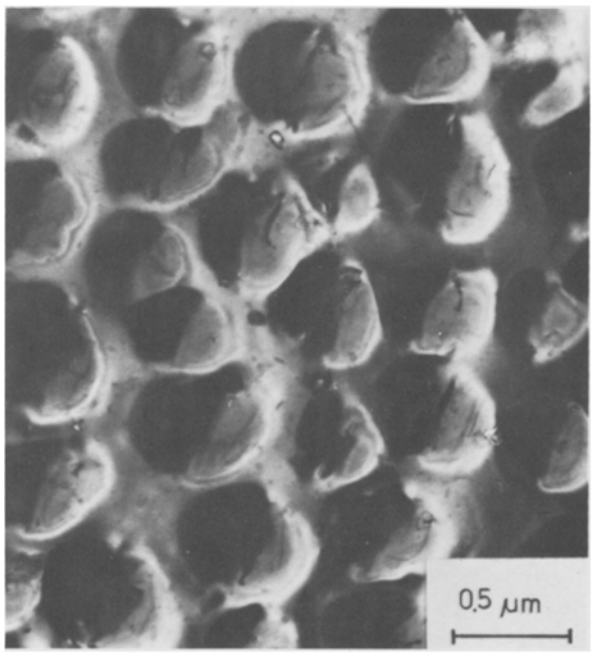

Fig. 4. TEM micrograph of a $Si_{0.75}Ge_{0.25}$ layer of 200 Å average thickness consisting of growth centres

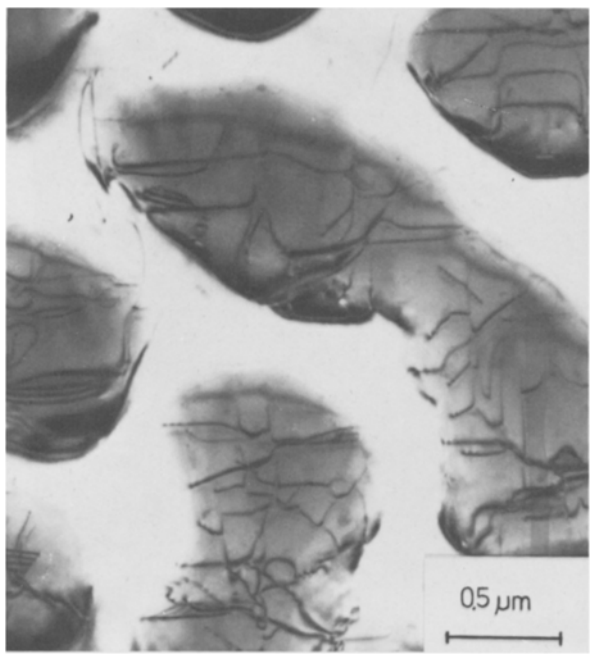

Fig. 5. TEM micrograph of a $Si_{0.75}Ge_{0.25}$ layer of 800 Å average thickness showing larger islands with dislocations

arrays more complicated than those of two-dimensionally grown layers. A $Si_{0.75}Ge_{0.25}$ layer of 5200 Å thickness is shown in Fig. 6. The islands have completely coalesced to a layer containing high density of complicately arranged dislocations and showing a rough surface.

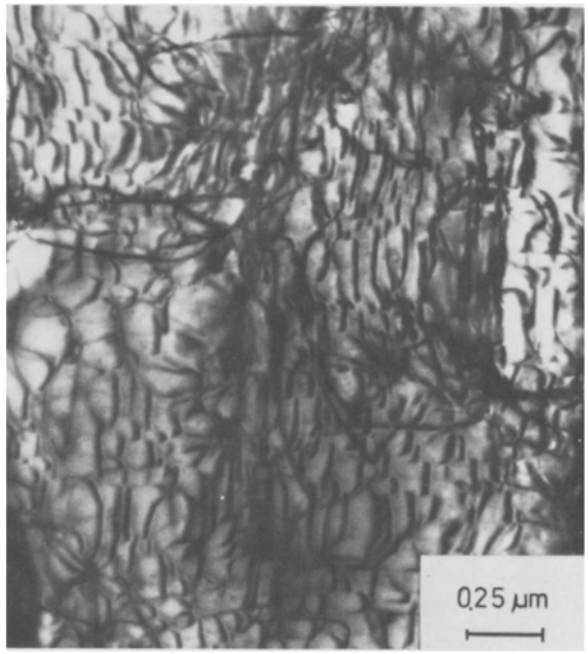

Fig. 6. TEM micrograph of a completely coalesced $Si_{0.75}Ge_{0.25}$ layer of 5200 Å average thickness showing a high density of complicately arranged dislocations

The condition of two-dimensional growth required for the epitaxy of superlattice structures could not be fulfilled for a Ge content of $\geqq 20$ at-%. Therefore Ge contents of 4–15 at-% were used for growing the following structures.

Van der Merwe [21] suggested a theoretical relation between the dislocation distance p and the thickness h of a heteroepitaxial layer and predicted pseudomorphic growth of thin films. In order to investigate pseudomorphic growth, $Si_{1-x}Ge_x$ layers were deposited with various thicknesses h and different values x. The x values were 0.04, 0.075, and 0.15 and the thicknesses h reached from 200 Å to 3 µm. Figure 7 shows the dislocation distance p (measured by means of TEM micrographs) as a function of layer thickness h for the different x values. The experimental points are mean values of dislocation distances because they considerably varied within each sample. The curves are in qualitative agreement with the calculated one after van der Merwe (compare Figs. 1 and 7).

$Si_{1-x}Ge_x$ films below the critical thickness h_c were found to be pseudomorphically grown and completely free of misfit dislocations. With increasing layer thick-

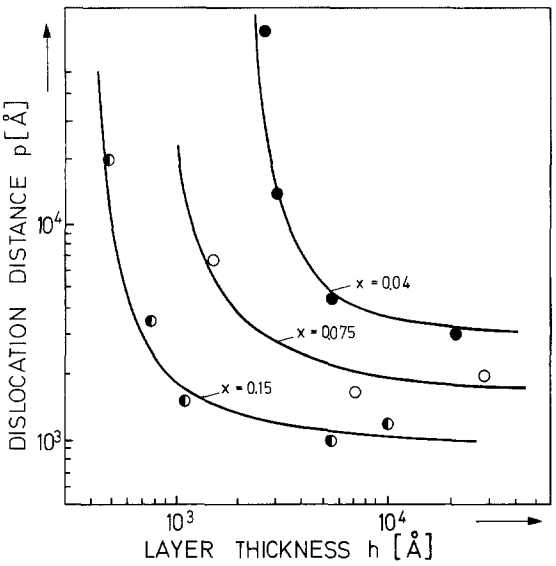

Fig. 7. Dislocation distance p versus thickness h of $Si_{1-x}Ge_x$ layers on Si substrate (experiment)

Table 1. Critical thickness h_c of $Si_{1-x}Ge_x$ layers with different Ge contents

Ge content x [at-%]	4	7.5	15
Lattice mismatch $\eta \cdot 10^{-3}$	1.6	3.0	6.0
Critical thickness h_c [Å]	2200	900	400

ness above h_c misfit dislocations are generated. The experimental determined values of the critical thickness h_c are listed in Table 1.

3.3 SiGe *Superlattice*

SiGe superlattice structures were grown at a substrate temperature of 750° C [23]. An alternating succession of $Si_{0.85}Ge_{0.15}$ films and pure Si films, both of the same thickness d, were deposited on Si substrate. Thus, the complete superlattice (thickness h) consisted of n ($n=1, 2, 3 \ldots$) $Si_{0.85}Ge_{0.15}$/Si periods with n ranging from 3 to 400. The thickness l of a period was varied from 100 to 800 Å ($l=2d$), i.e. the layer thickness d was smaller than the critical thickness h_c. Misfit dislocations forming a square grid pattern were observed in the superlattice. However, the misfit dislocations are confined to the first interfaces located near the substrate. The interfaces away from the substrate contain only few misfit dislocations. Thus, the mismatch accomodation within the superlattice is mainly (more than 99%) performed by elastic forces which is characteristic for pseudomorphic growth mode. The total misfit dislocation density depends on superlattice thickness h. Figure 8 shows the TEM micrograph of a SiGe superlattice of the thickness $h=1900$ Å ($n=5$, $l=380$ Å)

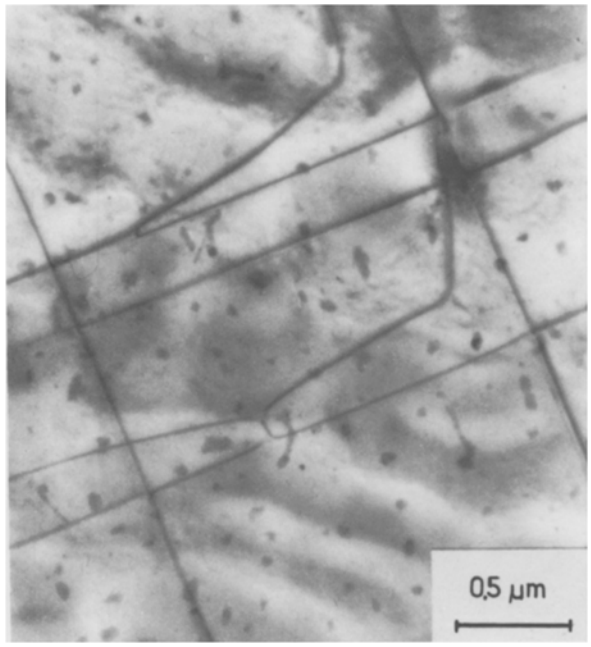

Fig. 8. TEM micrograph of misfit dislocations in a SiGe superlattice of the thickness $h=1900$ Å (5 periods of 380 Å)

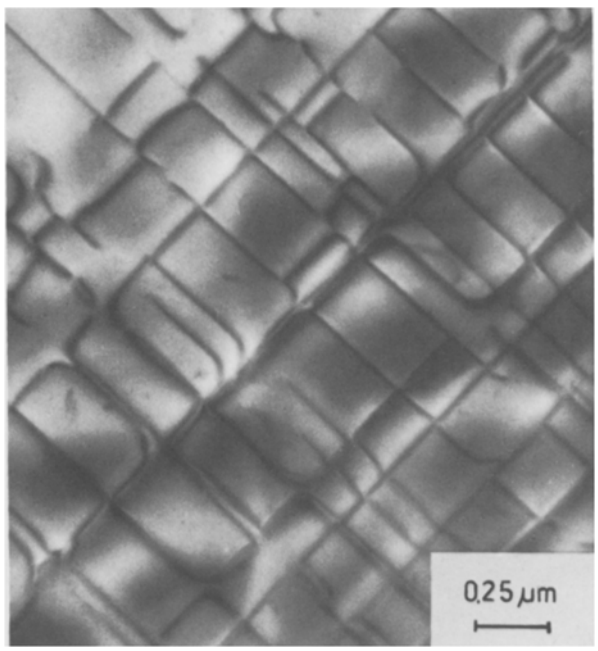

Fig. 9. TEM micrograph of misfit dislocations in a SiGe superlattice of the thickness $h=7200$ Å (20 periods of 360 Å)

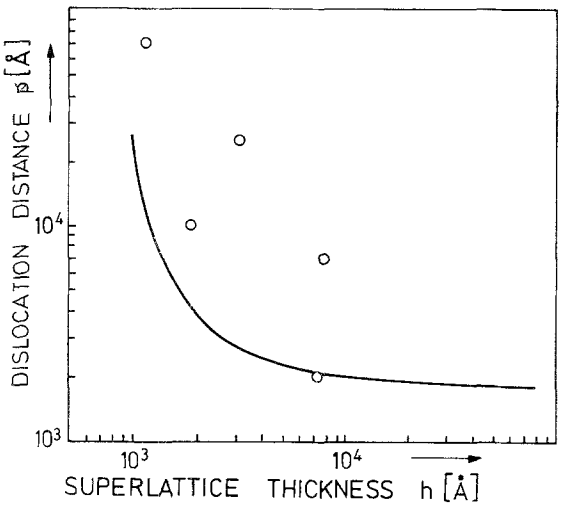

Fig. 10. Experimentally found dependence of dislocation distance p on SiGe superlattice thickness h. The periods of this superlattices range from $l=340$ Å to $l=400$ Å. The solid curve corresponds to the curve ($x=0.075$) of Fig. 7

and Fig. 9 that of a SiGe superlattice of the thickness $h=7200$ Å ($n=20$, $l=360$ Å). We measured the dislocation spacing as seen on TEM micrographs. The experimental results are shown in Fig. 10. The circles are the mean dislocation distances, and the solid curve corresponds to that curve of Fig. 7 which belongs to the Ge content $x=0.075$. We selected this curve of Fig. 7 for comparison because the SiGe superlattice and a $Si_{1-x}Ge_x$ layer with $x=0.075$ have the same Ge content. Figure 10 indicates that the misfit dislocation distance of the SiGe superlattice is equal to or larger than the misfit dislocation distance of a $Si_{0.925}Ge_{0.075}$ layer with the same thickness h. We assume that in thermodynamic equilibrium the superlattice shows the following behaviour: Only the interface between substrate and superlattice contains a net of misfit dislocations the density of which has the same dependence on thickness h as the density in a $Si_{1-x}Ge_x$ layer with the same net Ge content. The growth mode of the alternating layers is pseudomorphic and the superlattice itself is free of misfit dislocations.

4. Conclusion

Good quality epitaxy (single crystal, no interdiffusion, two-dimensional growth, almost pseudomorphic growth) of the SiGe superlattice is obtained by UHV evaporation technique at 750° C, a Ge content $x \leqq 0.2$, and a superlattice period $l \leqq 800$ Å.

The pseudomorphic growth mode of very thin heteroepitaxial layers predicted by van der Merwe is confirmed. The critical thickness connected with the generation of misfit dislocations is larger than calculated using van der Merwe theory presumably because the thermodynamic equilibrium in SiGe was not reached in spite of a slow growth rate.

Under our experimental conditions two-dimensional growth by motion of steps could be reached with a mismatch less than $8 \cdot 10^{-3}$. With mismatch above $8 \cdot 10^{-3}$ growth occured by three-dimensional nucleation and island growth.

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