Reduction of Threading Dislocation Densities in Heavily Lattice Mismatched PbSe on Si(111) by Glide

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(Received 9 September 1996)

Epitaxial PbSe layers on Si(111) relax nearly completely owing to the easy dislocation glide in the main $\{100\}\langle 110\rangle$ glide system. Threading dislocations introduced by the thermal mismatch strains are able to move distances of several cm and to escape at the edges of the samples. Etch-pit densities as low as 10^6 cm^{-2} were obtained in layers with a thickness of $d = 4$ μm. The etch-pit density scales with $1/d^2$, which may be understood as a consequence of the annealing step and of the high mobility of dislocations. By applying several anneal cycles, threading dislocation densities of essentially zero should result. [S0031-9007(97)02926-8]

PACS numbers: 68.55.Jk, 68.60.Bs

The reduction of threading dislocation (TD) densities in lattice-mismatched epitaxial layers has received considerable attention in recent years, especially for III-V and IV-IV semiconductors [1]. IV-VI layers like-narrow gap PbSe and $Pb_{1-x}Sn_xSe$ on Si substrates are of interest for infrared sensor device applications owing to the easy growth procedure and the potential to obtain high quality results despite the large lattice mismatch [2]. Crack-free layers are obtained by molecular beam epitaxy (MBE) on Si(111). Highest quality is obtained by using a thin (2 nm) intermediate CaF_2 buffer layer for compatibility reasons [3], but direct growth on Si is possible, too [4]. The lattice and, more important in this context, thermal expansion mismatch strain is relaxed by glide of dislocations in the main $\{100\}\langle 110\rangle$ glide system for these layers which have the NaCl structure. Figure 1 shows a schematic drawing of the glide and crystallographic geometry. Nearly complete strain relaxation is obtained in layers with a thickness of several μm, and on each temperature cycle, e.g., from room temperature (RT) to 80 K or vice versa. Even after more than 1400 such cycles, plastic strain relaxation still occurs on each temperature change, and it was estimated that the layers had undergone a cumulative plastic deformation exceeding 400% [3]. The structural quality (width of x-ray rocking curves or etch-pit densities) has changed only slightly after these procedures. Even higher quality is obtainable if the samples are annealed at 200–400 °C in vacuum or Se vapor, as indicated, e.g., by low temperature (below 10 K) mobilities as high as 250 000 cm^2/V s which are limited by defects. An estimate based on geometrical arguments and the above experimental findings was performed which predicted movements of the threading ends of misfit dislocations (MD) in the cm range in layers with dislocation densities of 10^8 cm^{-2} [5].

It is the purpose of this Letter to show that such large movements are indeed observed. This is different from III-V or IV-IV semiconductors, where only slight movements of TDs occur, and interactions of the glissile 60° dislocations soon lead to blocking even if the mismatch is small [1]. In addition, the scaling law for reduction of TD segments with thickness d in PbSe layers on Si(111) does not show the usual $1/d$ behavior characteristic for binary recombination [6,7], but the density ρ of threading ends decreases faster. This must be due to the extremely easy movement of the dislocations over large distances, which might even lead to virtually zero TD density after several annealing cycles.

For the experimental studies, Si(111) substrates with a miscut $<0.5°$ were used. A thin CaF_2 buffer layer with a thickness below the critical thickness for MD creation (2 nm at the growth temperature of 750 °C) was grown,

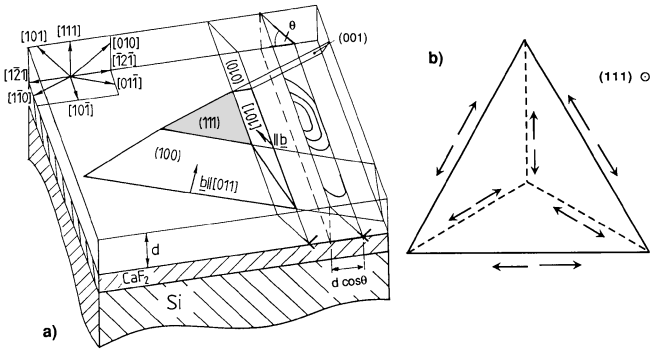

FIG. 1. Schematic drawing of the arrangement of the $\{100\}\langle 110\rangle$ glide system for the NaCl type PbSe(111) layers on Si(111). (a) Perspective drawing; (b) arrangement of possible $a/2\langle 110\rangle$-type Burgers vectors; dashed lines: Burgers vectors which are inclined to the interface and therefore belong to glissile dislocations.

and the wafer moved in vacuum to a second growth chamber where PbSe was deposited at about 400 °C from a single PbSe source. Growth starts by nucleation and islanding because of the high lattice mismatch between CaF_2 and PbSe (12%). Two-dimensional growth results after an initial layer of an average thickness of about 10 nm has formed. Typical layers were grown with a thickness ranging from 2 to 8 μm. All these layers show slip steps running along the three equivalent $\langle 110 \rangle$ directions of the intersection of the {100}-type glide planes with the surface, caused by those dislocations that have moved across the whole thickness of the layer. These slip steps, which are arranged with 3-fold symmetry, are revealed by Nomarsky light microscopy, or with (near) atomic resolution with scanning tunneling microscopy. Typical high-resolution x-ray diffraction (HRXRD) linewidths were in the range of 100 arcsec for layers 3 μm thick, and still lower for thicker layers [2,3].

Etch-pit densities of typical PbSe layers after growth with this thickness were 3×10^7 to 6×10^7 cm^{-2}. To demonstrate the easy mobility of threading ends, rectangular islands were etched into the layers. Figure 2(a) shows the etch-pit density of an island just after growth. A homogeneous distribution of etch pits is observed; the density is about 3×10^7 cm^{-2}. Similar islands of the same sample (but where no etch-pit treatment was applied) were then heated to 300 °C, and etched after cooldown to RT for etch-pit analysis. Figure 2(b) shows a micrograph of such an island. The most striking feature is the extremely reduced etch-pit density over most of its interior. On all such rectangular islands investigated, similar patterns were reproducibly observed. All showed the same features, a very low dislocation density in the interior, and an increased density along a U-shaped band located a few micrometers away from the edges. This band runs along three of the four edges only, while no increased density is observed along the fourth edge. This latter edge runs parallel to the $[10\bar{1}]$ direction formed by the intersection with the surface of the (010)-glide planes *inclined away* from the edge [i.e., the (010)-glide planes plotted in Fig. 1(a) with the island on the left]. On the other three edges with a different crystallographic orientation, a band with increased etch-pit density is observed [8]. The asymmetry

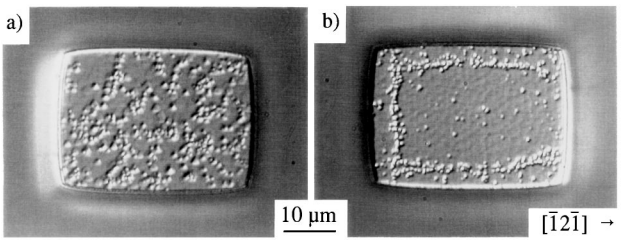

FIG. 2. Distribution of etch pits on rectangular PbSe(111) islands on Si(111) before (a) and after (b) a thermal cycle to 300 °C. The crystallographic orientation is plotted pointing into the same directions as in Fig. 1.

is correlated with the mechanical strain, which decreases to zero at the edges. For most orientations, it becomes too small near the edge to move the threading segment of the MD completely out of the island. Only for edges oriented along $[10\bar{1}]$ and with the (010)-glide planes inclined away as described above, the strain field is changing in a manner that the threading ends can escape completely. The exact nature of how this occurs is not yet analyzed, but is of no importance for the following.

To find out over which distances the threading ends of MDs are able to move subject to the thermal mismatch strain on annealing, islands or samples of different sizes have to be examined. A micrograph from the largest island studied, which had a size of 3 cm $\times$ 3 cm, is shown in Fig. 3. The edges of the island, which comprises the whole sample, were obtained by cleaving along the same directions as for the islands in Fig. 2. The sample was annealed for 2 h at 400 °C, cooled to RT, and etched for etch-pit analysis. Along the edge visible in the micrograph, a band with increased density is seen. Outside the band towards the edge, the PbSe layer is severely damaged owing to the cleaving of the substrate, and its surface morphology must be discarded. In the interior, as before, an extremely reduced etch-pit density is obtained. From a micrograph taken in the middle of the sample, the counted etch-pit density is 1×10^6 cm^{-2}. The same density is maintained over most of the sample size except in a band about 10 μm wide along the edges.

The decrease of dislocation densities (etch-pit densities) with increasing layer thickness is plotted in Fig. 4. Here, a similar sample was etched down to different thicknesses and annealed, and the revealed etch pits in the interior of the samples were counted. With increasing thickness, the TD density at the surface of the layer decreases with approximately the *square* of the thickness d. This is different from III-V or IV-IV semiconductors, where a $1/d$ scaling is observed, or even a leveling off of the density for thicker layers [7]. The $1/d$ dependence can be understood as the probability that two TDs meet during growth in order to annihilate is proportional to ρ^2 [6,7], i.e., a binary recombination law.

The near $1/d^2$ dependence found in the present study for annealed PbSe must be explained as follows: For a certain grown layer with thickness d (and before performing anneals or temperature changes), the TD density acquired during growth scales with $1/d$ as described above. When changing the temperature (after growth is completed), one has to take into account that each threading end of the MD is able to glide along the whole layer dimension. If this TD does not encounter and react with any other TD on its glide across the whole sample, no change in the $1/d$ dependence results. However, assuming that this moving threading end encounters another threading end and reacts (annihilates or fuses) with it, a further dislocation reduction takes place. Remembering that all TD behave in this manner, the result must be that

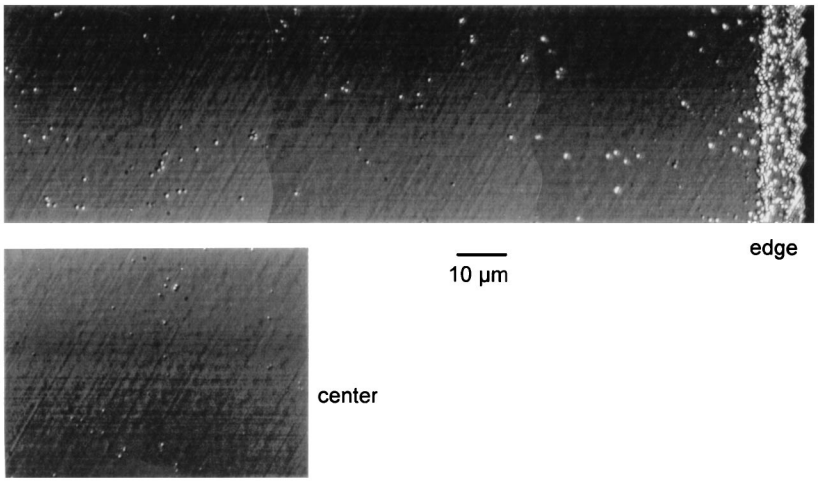

FIG. 3. Distribution of etch pits in a 3×3 cm^2 and 4 μm thick PbSe(111) layer on Si(111) after 2 h anneal at 400 °C. Top: etch-pit distribution near the edge; bottom: etch-pit distribution in the middle of the sample. The etch-pit density is 1×10^6 cm^{-2} in the interior of the sample.

this reduction again scales with $1/d$ in order to finally achieve the observed $1/d^2$ dependence.

An explanation of this dependence has to take into account the inhomogeneous distribution of dislocations across the layer thickness. The junctions where two threading ends have reacted in the interior of the layer (and with no or just one threading segment left which extends to the surface) may be able to move further towards the interface as long as the dislocation density is low. Near the interface, the dislocation density increases and the junctions encounter more obstacles to move down. Thus, a higher decrease of the dislocation density is possible closer to the surface.

It seems to be the first time that such a dependence has been observed. Clearly, a $1/d^2$ dependence as compared to a $1/d$ dependence leads to a faster decrease of dislocation density with increasing layer thickness, which is of value for growth of layers with very low dislocation density. The exact nature of the dislocation interactions for these NaCl-type semiconductors is not known and deserved further studies.

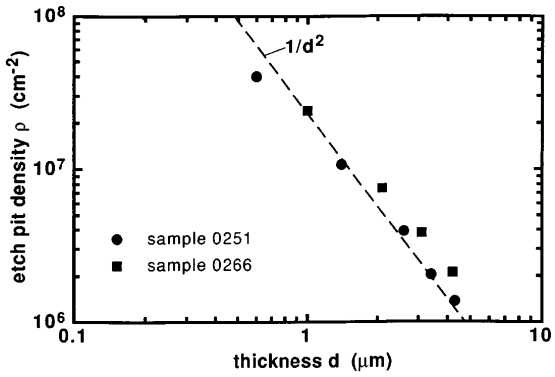

FIG. 4. Etch-pit density in PbSe(111) on Si(111) vs thickness d of the layers (points). A $1/d^2$ dependence is indicated by the dashed line.

If further temperature anneals are applied to the same sample, existing threading segments will again start to move across the layers, or new TD/MDs form as soon as the thermal mismatch strain exceeds a certain value. However, all these threading ends remain extremely mobile and can again cross the whole sample with cm size. By annealing at high temperatures (say, e.g., 300 °C) we always observed an increase in structural quality, i.e., an increase of the saturation Hall mobility at low temperatures with a corresponding decrease of TD densities [9]. By applying numerous cycles from RT to cryogenic temperatures and vice versa, however, a slight increase in ρ after many temperature cycles and some strain hardening was observed [3]. The properties are restored towards the original values by a high-temperature anneal.

The $1/d^2$ law is valid, however, only if it is assumed that all or most the TDs are involved in reactions. Otherwise, a weaker dependence on d would result. The $1/d^2$ law might therefore become invalid for very low dislocation densities or if the TDs do not move over large enough distances (e.g., if the temperature changes are too small to induce enough mismatch strain, or if too many defects pin the MD/TDs).

In addition to the mobile dislocations, sessile dislocations are present ("sessile" means in this context that the Schmid Factor is zero). Sessile TDs (as well as glissile ones) are expected to be formed during the first stages of growth at least where the islands coalesce. We will show in the following that mobile as well as sessile dislocations can be reduced further by temperature changes. A threading end of a MD which glides and meets on the same plane the threading end of another MD can join with this latter threading end, i.e., a single, but longer MD is formed. This happens if both MD have the same Burgers vector. Contrary, two TDs with opposite Burgers vectors which meet annihilate. What happens to two threading ends which meet if none of these conditions for the

Burgers vectors is fulfilled is at first glance not of importance as long as such an encounter does not lead to a blocking of further movement or to a dislocation multiplication. However, additional dislocation reduction results in certain cases: Assume for the moment that a glissile TD sweeps in the thermal mismatch strain field and encounters a sessile TD which has its Burgers vector parallel to the interface plane [see Fig. 1(b) for the 12 possible directions of $a/2\langle 110\rangle$ type Burgers vectors]. A probability exists that a reaction which leads to a fusion occurs; i.e., a single new dislocation with $a/2\langle 110\rangle$ type Burgers vector forms. One possibility for this (which can occur on a short line element parallel to [001]) is

$$\text{Glissile TD } (g)\text{: } b_1 = a/2[101],\ \text{glide plane } (010)\,;$$

$$\text{Sessile TD } (s)\text{: } b_2 = a/2[\bar{1}10]\,;$$

$$\text{Fusion: } b = b_1 + b_2 = a/2[011],\ \text{glide plane } (100)\,.$$

A glissile TD has therefore reacted (fused) with a sessile TD to form a new glissile TD: $g + s \rightarrow g$. In a similar way, one finds reactions for $g + g \rightarrow s$. But since $g + s \rightarrow g$ from above, three glissile TDs are reduced to one glissile TD in the end. Since new glissile threading ends form upon each significant temperature change in order to relieve the thermal mismatch strain, a sufficient number of glissile TDs is always available to reduce the TD density. Reactions of the type $g + g \rightarrow s$ (in our notation) have indeed been observed with transmission electron microscopy [10] in $PbTe/Pb_{1-x}Sn_xTe(111)$, and, very recently, with scanning tunneling microscopy in EuTe/PbTe(111) heteroepitaxial systems [11]. These reactions have never been claimed to be important for the reduction of dislocation densities, however.

Multiple application of temperature changes (anneals) can therefore cause a further reduction in the density of sessile TDs. There is no hindrance that after many such anneals virtually zero TD density could be obtained. As described above, we have actually observed such further reductions, but have not yet explored the full potential of this method to obtain layers with essentially zero TD density. The method seems to be applicable to other NaCl-type semiconductors with {100} glide planes and where near no dislocation blocking occurs, but not for zinc blende type semiconductors due to the different dislocation behavior in these systems. It is essential that the primary glide planes are {100} for the considered NaCl type layers. If the primary glide planes are {110} (as for NaCl-type materials with high ionicity), the displacements (combinations of jogs and kinks) formed in mutually intersecting dislocations are not glissile because the jogs may lie in {100} planes which are not easily activated for glide [12]. However, NaCl-type materials with low ionicity as PbSe glide on {100} planes. In this case, the resulting jogs lie in {100} planes as well and can therefore glide with the dislocations.

In conclusion, we have shown that in PbSe(111) layers on Si(111) substrates TD densities as low as 10^6 cm^{-2} are obtained, and the threading ends of MDs are extremely mobile and can glide on their main {100} glide planes across complete samples of a size of several cm. This is due to an extremely low interaction probability for the blocking of further dislocation motion. This high dislocation mobility has the effect that the TD density decreases with the square of the layer thickness. Multiple anneals lead to still further reduction of TD densities. Since sessile TDs can convert to glissile TDs by dislocation reactions upon temperature change, each anneal reduces the TD density further; it even seems possible that epitaxial layers with high lattice mismatch can be obtained which are completely free of TDs.

Financial support by the Swiss National Science Foundation and the Swiss Defence and Procurement agency is gratefully acknowledged.

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