Elimination of threading dislocations in as-grown PbSe film on patterned Si(111) substrate using molecular beam epitaxy

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A high-quality as-grown PbSe film with a record low threading dislocation density of 9×10^5 cm^{-2} on patterned Si(111) substrate has been obtained using molecular beam epitaxy. The mechanisms leading to the remarkable reduction in threading dislocation density are analyzed. Based on the analysis, further reduction in dislocation density is anticipated. Materials with such low dislocation density should significantly improve the Si-based IV-VI group device performance. © *2010 American Institute of Physics*. [doi:10.1063/1.3457863]

Heteroepitaxy of lead salt films like PbSe and $Pb_{1-x}Sn_xSe$ have widespread applications in solid state devices such as mid-infrared (IR) light-emitting and laser diodes,[1,2] mid-IR sensors,[3] and thermoelectric coolers and power generators.[4] Their growth on Si substrates has attracted great interest due to the availability and scalability of Si substrate, and the integration with silicon-based integrated circuits (IC). Because of the primary $\{100\}\langle110\rangle$ dislocation glide system, epitaxial growth on Si(111) has been proven to produce the best material quality.[5] However, high threading dislocation densities of the as-grown lead salt epilayer via molecular beam epitaxy (MBE) in the range of $3\times10^7-1\times10^8$ cm^{-2} still limit device performance. By *ex situ* temperature cycling, the dislocation density can be reduced by over an order of magnitude[6] but the process could contaminate the epitaxial film. Therefore, developing a growth method via MBE that could significantly reduce the dislocation densities in the as-grown films is of critical importance for lead salt device fabrication.

Recently, a record low threading dislocation density of 9×10^5 cm^{-2} of as-grown PbSe film on patterned Si(111) using MBE has been achieved in our laboratory.[7] So far, this is the lowest dislocation density reported of all mid- and long-wave semiconductor materials grown on Si substrates. However, the mechanisms causing dislocation reduction on patterned substrate have not been discussed. Thus, in this paper, those mechanisms for reduction in threading dislocation in PbSe film grown on patterned Si(111) substrate will be analyzed.

In the experiment, 1×1 cm^2 Si(111) substrate was patterned before growth to produce matrix of 5×5 holes. Then Si substrate was dry etched using a deep reactive ion etching system to produce the pattern with etch depth of 3 μm. The patterned Si substrate and another 1×1 cm^2 unpatterned Si substrate were cleaned with a modified Shiraki cleaning method. A custom-designed two-chamber MBE system was used for the growth. A CaF_2 layer of 2 nm that is within the critical thickness was grown as a buffer layer in one chamber. PbSe thin films were then grown on the CaF_2/Si substrates in another chamber without breaking the vacuum. The substrate temperature remained at 420 °C during the growth. The thickness of the PbSe epitaxial layer was 1.8 μm measured by scanning electron microscopy (SEM).

A wet chemical etching process following Ref. 8 was then undertaken to reveal threading dislocations of the PbSe films as etch pits on both patterned and unpatterned substrates. Figure 1 shows the top view SEM image of PbSe film grown on patterned Si(111) substrate after wet chemical etching process. The minimum edge-to-edge spacing between adjacent holes is 1.5 μm. The unpatterned spacing from the side of patterned hole to the edge of the substrate is about 5 mm, which is intentionally designed to compare with the growth on unpatterned substrate. This spacing area is marked as area 1. The film grown on patterned structure is marked as area 2. Close-up SEM images in Figs. 2(a) and 2(b) were taken in both areas.

Figure 2(a) is the SEM image inside the area 1 that shows etch pits of triangle shape for the PbSe film grown on Si(111) substrate. The etch pit density (EPD) in area 1 is counted to be around 1×10^8 cm^{-2}, which is consistent with the result obtained from the PbSe film grown on unpatterned substrate in the same MBE run. However, the EPD in area 2 is significantly lower than that in area 1. Many of the periodic elements in area 2 are free of etch pits. Figure 2(b) shows the SEM image from the center of area 2. There is only one etch pit observed and thus the EPD is calculated to

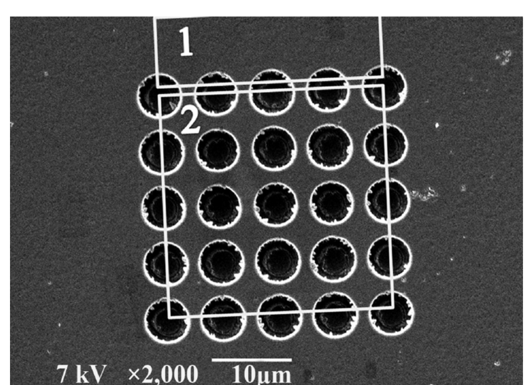

FIG. 1. Top view SEM image of 5×5 holes after PbSe growth and chemical wet etching process.

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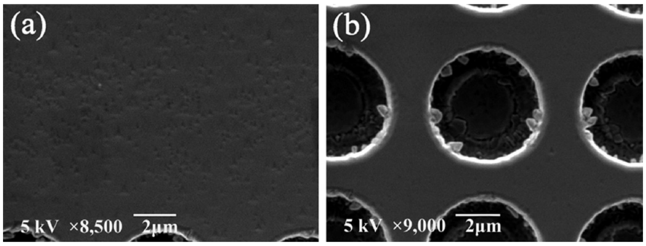

FIG. 2. Close-up top view SEM images of Fig. 1: (a) in area 1; (b) in the center of area 2.

be 9×10^5 cm^{-2}. The mechanisms causing this significant dislocation reduction will be discussed as follows.

It is well known that the strain induced by misfit in IV-VI material on Si(111) substrate is mainly relieved through glide of dislocations in the $\{100\}\langle110\rangle$ glide system.[5] Also, it has been predicted that most threading ends remain extremely mobile and can cross the whole sample with cm size by applying temperature cycles.[6,9] However, the number of threading dislocations that can be removed by glide in IV-VI material has not been analyzed, while a similar issue in III-V material system has already been discussed.[10]

In IV-VI material system, the average separation of parallel misfit dislocations is intercorrelated with the plastic strain ε and is given by $s=3/2b_{\text{eff}}\varepsilon^{-1}$, where $b_{\text{eff}}\sim2.5$ Å is the projection of the Burgers vector responsible for strain relief.[9] Here, the side length L of the sample is assumed to be parallel to the glide direction $\langle110\rangle$. If all threading dislocations glide to the sample edge, then the average length of misfit dislocation is L/2. If the number of threading dislocations per unit area is ρ, then it follows from geometry for threefold symmetry $sL\rho=6$.[9] Thus, the density of threading dislocations that can be removed by glide is $\rho=4\varepsilon/(b_{\text{eff}}L)$. Therefore, its upper limit is obtained by setting ε equal to the misfit f and expressed below

$$\rho_{\max}=\frac{4f}{b_{\text{eff}}L}.$$

For our samples, L is 4.5 μm for PbSe film on patterned Si(111) which is the maximum edge to edge spacing between adjacent holes, and 1 cm for PbSe film grown on the unpatterned Si(111). For PbSe grown on Si(111), the induced lattice misfit strain is ~12% at growth temperature and thermal mismatch strain created by temperature change from growth temperature to room temperature is ~0.87%. The calculated upper limits to the density of threading dislocations that can be removed by glide for the PbSe samples on patterned and unpatterned Si(111) are listed in Table I.

These upper limits were calculated by assuming that the PbSe was fully strained. In reality, most of the strain due to lattice mismatch is relaxed for layers thicker than the critical thickness which is ~2.6 nm. Therefore, the actual limits to the density of threading dislocation that can be removed by glide due to lattice mismatch strain should be less than that listed in Table I for both cases. Thus, the thermal mismatch strain could be dominating. Nonetheless, no matter which strain is dominating, it is clearly shown that the upper limit for PbSe on patterned Si (111) is of over three orders of magnitude larger than that for PbSe on the unpatterned Si (111). The EPD of *in situ* grown PbSe films on the unpatterned Si(111) is typically in the range of $3\times10^7-1\times10^8$ cm^{-2}, which is an indication that above mentioned mechanism will not be able to reduce dislocation to below 10^7 cm^{-2}. On the contrary, the PbSe film on patterned Si(111) is capable of removing the mobile threading dislocations higher than 10^9 cm^{-2} by glide. This offers an explanation of the low EPD we reported in this paper.

TABLE I. The upper limits of threading dislocation density removed by glide.

PbSe films on	Upper limits due to (cm^{-2})		
	Lattice misfit	Thermal mismatch	Total
Patterned Si	4.5×10^{10}	2.3×10^9	4.73×10^{10}
Unpatterned Si	2.0×10^7	1.1×10^6	2.31×10^7

This result could also be used to explain the reported *ex situ* high temperature cycling process to reduce dislocation density for IV-VI films on planar Si(111).[6] As additional stresses build up during the temperature cycle, according to the above analysis, the density of threading dislocation that can be removed by glide increases linearly with the strain induced.

However, introducing additional stresses by applying numerous temperature cycles also increase the threading dislocation density ρ in planar epitaxial PbSe on Si(111),[5,6] which suggests that certain dislocation nucleation sources are activated. For the growth on patterned substrate, we believe that the lateral dimension related nucleation sources will be suppressed. This is another important mechanism for reduction in threading dislocation density. The lateral dimension dependent dislocation nucleation sources include dislocation multiplication by threading dislocation interaction, and surface dislocation nucleation generated by thermal mismatch strain.

First of all, dislocation multiplication is one of the major dislocation nucleation mechanisms that has been researched in detail.[10,11] Matthews *et al.*[10] indicated that the conditions to prevent multiplication are those that avoid interaction of threading dislocations. If the threading ends of two dislocations moving in different glide planes encounter, the geometrical probability for one moving threading dislocation meets another threading dislocation is given by $pl=1/\rho$, where l is the mean free path of a threading dislocation, and $p=t\sin\theta$ is the width of the glide plane projection with layer thickness t and the angle θ between the (100) glide plane and the normal to the interface plane. The calculated mean free path is 0.375 μm for the PbSe film grown on Si(111). Assuming one threading dislocation glides through one edge to another, the dislocation interactions will happen 12 times for the sample grown on patterned Si(111). However, for the 1×1 cm^2 sample grown on unpatterned Si(111), the interaction will be 2.7×10^4 times, which is three orders of magnitude larger than that on patterned Si(111). It means that the dislocation multiplication would be extremely rare and dislocation escape would be common in the film grown on patterned Si(111), in contrast to the film on unpatterned Si(111).

Second, thermal residual stress is another lateral dimension dependent dislocation nucleation mechanism. It is well known that PbSe material has much larger thermal coefficient than Si, therefore, the thermal mismatch would induce huge residual stress after growth of PbSe film on Si substrates. As a result, considerable dislocations will form to relieve the stress. Here, we applied a model to explain the effect of edge-to-edge spacing reduction to thermal stress,[12] which has been proven to be valid in epitaxial III-V material systems.[13] Thermal residual stress in the epitaxial film can be expressed as follows:

$$\sigma(x) = \sigma_0[1 - e^{-k(l/2-x)}],$$

with

$$\begin{cases} \sigma_0 = \dfrac{\Delta\alpha\Delta T}{\lambda t_{\mathrm{PbSe}}}\left[1 + \dfrac{3(t_{\mathrm{PbSe}} + t_{\mathrm{Si}})D_{\mathrm{PbSe}}}{(D_{\mathrm{PbSe}} + D_{\mathrm{Si}})t_{\mathrm{PbSe}}}\right] \\ \lambda = \dfrac{1}{12}\left[\dfrac{t_{\mathrm{PbSe}}^2}{D_{\mathrm{PbSe}}} + \dfrac{t_{\mathrm{Si}}^2}{D_{\mathrm{Si}}} + \dfrac{3(t_{\mathrm{PbSe}} + t_{\mathrm{Si}})^2}{D_{\mathrm{PbSe}} + D_{\mathrm{Si}}}\right] \\ k = \sqrt{\dfrac{2\lambda}{3}\left(\dfrac{1+\upsilon_{\mathrm{PbSe}}}{lE_{\mathrm{PbSe}}} + \dfrac{1+\upsilon_{\mathrm{Si}}}{lE_{\mathrm{Si}}}\right)} \\ D_i = \dfrac{E_i t_i^3}{12(1-\upsilon_i^2)} \end{cases},$$

where $\Delta\alpha$ is the difference of thermal expansion coefficient between PbSe and Si, ΔT is the variation between growth and room temperature, E is Young's modulus, t is the thickness, υ is Poisson's ratio, l is the lateral edge-to-edge width, and x is the distance from the center of patterned film, respectively. Calculated results show that the average thermal stress for the film grown on unpatterned Si(111) is 4.4×10^8 Pa, and that for the film on patterned Si(111) is 1.6×10^8 Pa. All material parameters are taken from Ref. 5, and Young's modulus and Poisson's ratio are calculated by the theory from Ref. 14. It was found that the square-root relationship between film stress and dislocation density in rocksalt structure crystals can be expressed as follows:[15]

$$\sigma = A\sqrt{N_d},$$

where A is a constant, N_d is measured dislocation density. Since such thermal stress created by patterned structure decreases three times, the dislocation density generated by such thermal residual stress should be almost an order of magnitude lower on patterned substrate than that on unpatterned substrate.

In summary, with the combination of the promoted dislocation glide and reduction in dislocation multiplication, the dislocation density on patterned substrate can be significantly reduced as evidenced by our experimental result of 9×10^5 cm^{-2}. Optimization of the pattern parameters could lead to further dislocation reduction. Epitaxial films with such low dislocation density should have significant implications for device fabrication on Si. The growth method could also be applied to other material systems grown on Si.

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