Molecular beam epitaxy growth of PbSe on BaF_2-coated Si(111) and observation of the PbSe growth interface

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Epitaxial growth of $PbSe/BaF_2/CaF_2$ heterostructures was carried out by molecular beam epitaxy (MBE) on Si(111) wafers. Successful transfer of 3-μm-thick PbSe epilayers was accomplished by bonding the MBE-grown samples face down to polished copper plates followed by the removal of the silicon substrate by dissolving the BaF_2 buffer layer in water. High-resolution x-ray diffraction measurements demonstrated that the PbSe epilayer maintained high-crystalline quality after transfer. In addition, optical Nomarski characterization of the exposed growth interface showed sets of parallel straight step lines consistent with glide of dislocations in the primary {100}⟨110⟩ glide system. Such features are evidence of the large thermal expansion mismatch strain that occurred in these layers. © *1999 American Vacuum Society.* [S0734-211X(99)03803-2]

I. INTRODUCTION

Recently, high-quality epitaxial growth of PbSe and related materials on (111)-oriented Si substrates has been accomplished by incorporating thin intermediate BaF_2/CaF_2 buffer layers.[1,2] Heteroepitaxial growth of PbSe on silicon takes advantage of silicon integration technology to obtain inexpensive photonic devices. Infrared sensor arrays with 3–12 μm cutoff wavelengths in PbSe and PbSnSe layers grown heteroepitaxially on Si(111) have been fabricated.[3] It is known that CaF_2 has a well-matched lattice constant with Si and BaF_2 has a well-matched lattice constant with PbSe. Furthermore, the thermal expansion coefficients of both BaF_2 and CaF_2 are very close to those of PbSe. In this system, BaF_2/CaF_2 buffer layers play a key role in the high-quality epitaxy of PbSe on Si substrates. However, the lattice misfit between BaF_2 and CaF_2 is as high as ~14%. The differences in thermal expansion coefficients between the $PbSe/BaF_2/CaF_2$ epilayers and the Si substrate are as large as 700%. Therefore, when $PbSe/BaF_2/CaF_2$ are epitaxially grown on Si(111) substrates large mechanical strains are expected on cooling down from growth temperature to room temperature. This strain is tensile because PbSe and the fluoride buffer layers contract considerably on cooling while the Si substrate with its much smaller thermal expansion coefficient impedes this process. Most of the lattice-misfit and thermal-mismatch strains are relaxed by the formation and movement of dislocations in the (111)-oriented fluoride buffer layers.[4] As a result, a high density of dislocations in the BaF_2/CaF_2 buffer layer and at the $PbSe/BaF_2$ interface was observed.[5,6]

In addition, BaF_2 and CaF_2 are insulators, which prevents electrical contact to the PbSe epilayer through the substrate. Hence, it is highly desirable to remove the BaF_2/CaF_2 buffer layers and the Si(111) substrate from the molecular beam epitaxy (MBE) grown IV–VI epilayers and transfer the PbSe epilayers to a material that has a better thermal expansion match and good thermal and electrical conductivities for possible regrowth of PbSe-related heterostructure devices. In this work, $PbSe/BaF_2/CaF_2$ heterostructures were grown by MBE on Si(111) substrates. The transfer of the PbSe epilayer to copper plates has been successfully accomplished by bonding followed by removal of the BaF_2/CaF_2 buffer layer and the Si(111) substrate. High-resolution x-ray diffraction (HRXRD) and surface profiling were used to study the quality of transferred PbSe/PbEuSe epilayers. The PbSe growth interface was characterized by parallel step lines indicating glide of dislocations in the primary {100}⟨110⟩ glide system.

II. EXPERIMENTS

A. MBE growth of $PbSe/BaF_2/CaF_2$

Growth of $PbSe/BaF_2/CaF_2$ on Si(111) was carried out in an Intevac Modular GEN II MBE system. 3-in.-diam p^+-type (0.005–0.025 Ω cm) Si wafers with off-cut angles less than 0.3° were cleaned using a modified Shiraki method followed by dipping in a HF solution. Adding this dipping step allows reduction of the Si thermal cleaning temperature by more than 300 °C so that unwanted reactions between Se and Si are avoided.[1] Si wafers were outgassed in the buffer chamber at 200 °C for 1 h before they were loaded into the growth chamber.

CaF_2 and BaF_2 growth was accomplished by heating high-purity polycrystalline CaF_2 and BaF_2 in dual-zone effusion cells held at 1270 and 1165 °C, respectively. The corresponding growth rates were about 8 Å/min for CaF_2 and 40 Å/min for BaF_2 as determined from reflection high-energy electron diffraction (RHEED) intensity oscillations and ellipsometry measurements. PbSe growth was accomplished by heating bulk PbSe in a low-temperature effusion cell. The effusion cell temperature was adjusted in the range of 635–710 °C to give a beam equivalent pressure (BEP) of 1.3×10^{-6} Torr and a growth rate of about 0.8 μm/h. PbEuSe growth was accomplished by evaporating bulk PbSe and elemental Eu from low-temperature effusion cells. A Eu flux

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rate of less than 1% of that of PbSe was used during the growth of the PbEuSe layer.

A 20-Å-thick CaF_2 layer was first grown on a thermally cleaned Si(111) substrate at 700 °C followed by a 6000-Å-thick BaF_2 layer grown at 320 °C. The growth of BaF_2/CaF_2 on Si(111) proceeds via a two-dimensional mode evidenced by (1×1) RHEED patterns. It was found in the experiment that in order to keep the surface normal of the PbSe layer the same as that of the underlying BaF_2/CaF_2/Si(111), a thin PbEuSe (~100 Å, with Eu content ≤1%) layer needs to be grown on the BaF_2/CaF_2/Si(111) prior to growing the PbSe layer.[7] Both the PbEuSe and 3-μm-thick PbSe layers were grown at a substrate temperature of 300 °C. For convenience in the following discussion, the thin PbEuSe layer is treated the same as PbSe because the Eu concentration is less than 1%.

B. Transfer of PbSe epilayer to copper

Selecting an appropriate alternative substrate material that mechanically supports lifted-off PbSe epilayers is important to the successful transfer and possible regrowth on the PbSe epilayer. The substitute substrate should have the following properties: (1) a thermal expansion coefficient close to that of PbSe; (2) a high thermal conductivity to dissipate the heat generated in devices; and (3) a high electrical conductivity. Copper is a material that satisfies the above three conditions.[8]

The first step in transferring the PbSe epilayer to copper substrates was bonding the MBE-grown layers to polished copper plates. Bonding materials are usually hard solders, soft solders, as well as metal-filled epoxies. Hard solders, including Au–Si, Au–Ge, and Au–Sn,[9] have high strength, which can produce high stresses in bonded films. Thus, for a PbSe epilayer, which is soft, the bonding PbSe could easily crack. So, the hard soldering technique is not suitable for PbSe bonding. It is known that indium (In) is soft and has good wetting properties on both copper and gold, which ensures good adherence of the epilayer to the copper plate through the In bonding medium. Furthermore, In has a relatively low melting temperature, 156.6 °C, and is a common bonding medium for IV–VI optoelectronic device packaging. It is expected that very little extra strain will be introduced into the PbSe epilayer after transfer. Indium solder was, therefore, selected to bond PbSe layers to copper.

The bonding procedure for PbSe films was as follows: as-grown samples were first coated with a 60-nm-thick thermally evaporated chromium film, then coated with a 150-nm-thick thermally evaporated Au layer. Polished and cleaned Cu plates were electroplated with ~2-μm-thick Au layer. The Au-electroplated Cu plates were heated in air to the In melting point and coated with a thin film of In. The Au-coated PbSe sample was then placed face down on the heated Cu plate to form an assembly, which was then cooled down to room temperature.

Following bonding, the assembly was immersed in deionized water to dissolve the BaF_2 buffer layer. It took several days for the BaF_2 buffer layer to be completely dissolved so that the Si substrate could be removed, while leaving the PbSe epilayer on the Cu plate. The transferred layers were mirror-like and optical Nomarski microscopy observation showed a smooth, crack-free surface.

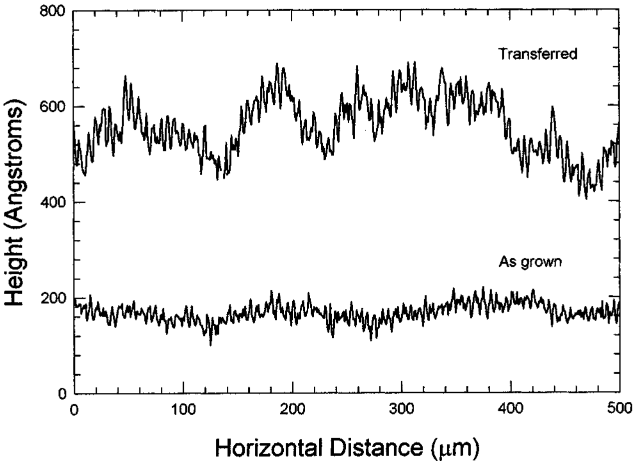

FIG. 1. Surface scan profiles for an as-grown PbSe/BaF_2/CaF_2 heterostructure and an exposed PbSe growth interface after transfer to a copper plate.

III. RESULTS AND DISCUSSION

A. Surface roughness

The surface roughnesses of as-grown and transferred layers were measured using a Tencor P-1 long scan profiler. Figure 1 compares the exposed growth interface of a transferred PbSe epilayer, and its as-grown surface before transfer. The typical peak roughness of the PbSe growth interface is about 240 Å, which is higher than the roughness of the as-grown PbSe surface, ~120 Å. Factors contributing to surface roughness of the bonded PbSe include a rough BaF_2 surface during MBE growth,[10] defects due to misfit dislocations, a rough Cu plate surface, which had a typical roughness of about 800 Å, and grain formation in the In–Au alloys underneath the bonded PbSe.

B. X-ray diffraction

Figure 2 displays $\omega/2\theta$ X-ray diffraction spectra for both an as-grown PbSe/BaF_2/CaF_2/Si(111) heterostructure and the transferred PbSe epilayer. The as-grown PbSe/BaF_2/CaF_2/Si(111) heterostructure, curve (a), shows peaks for PbSe (PbEuSe-related peaks were not resolved from PbSe peaks because of its good lattice match with PbSe), BaF_2 and Si. The inset represents a high-resolution scan of the (222) peak. The full width at half maximum (FWHM) of the PbSe peak is 191 arcsec, which indicates its good crystalline quality. The diffraction from the CaF_2 buffer layer was not observed because it is only about 20 Å thick. Curve (b) in Fig. 2 shows the x-ray diffraction spectrum for the PbSe epilayer transferred to a Cu plate. Note the complete absence of peaks associated with BaF_2 and Si. The FWHM of the bonded PbSe epilayer is 222 arcsec, showing that the crystalline quality of the PbSe epilayer after transfer has changed only

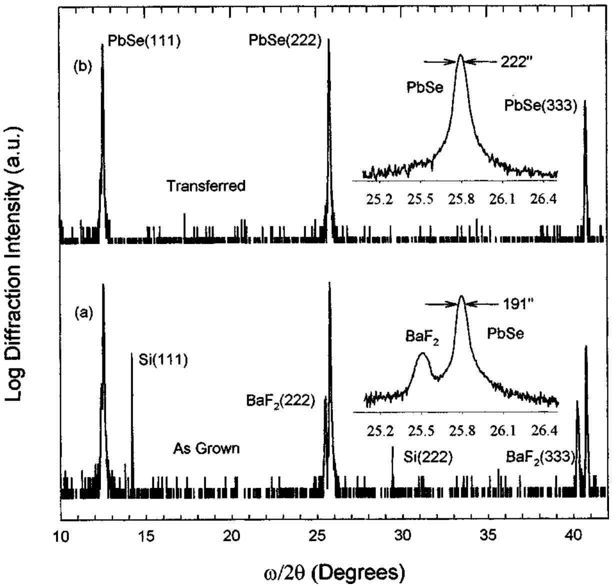

FIG. 2. High-resolution x-ray diffraction spectra, ω–2θ, for an as-grown $PbSe/BaF_2/CaF_2/Si(111)$ heterostructure (a) and a PbSe epilayer after transfer to a copper plate (b). The insets display the FWHM of both the as-grown structure and the transferred PbSe epilayer. Note the complete absence of BaF_2 and Si peaks for the transferred layer.

slightly after epilayer transfer. The slight FWHM broadening of the transferred PbSe is likely due to the fact that the exposed growth interface possibly contains a higher density of misfit dislocations associated with the ~1% lattice mismatch with BaF_2 and the 600% thermal expansion mismatch with the Si substrate. Indeed, the expectation of a higher density of misfit dislocations at the PbSe growth interface was confirmed by the observation of optical Normarski microscopy, which will be discussed in the next section.

C. Observation of the PbSe growth interface

$PbSe/BaF_2/CaF_2/Si(111)$ heterostructures represent a heavily lattice- and thermal-expansion-mismatched materials system. The lattice mismatch between the silicon substrate and CaF_2 is 0.6% at room temperature and 2.4% at 700 °C growth temperatures. These lattice mismatches are overcome by generation of glissile dislocations with Burgers vectors inclined to the interface in the $\{100\}\langle 110\rangle$ primary glide system.[5] The lattice constant of BaF_2 is 14% larger than CaF_2 at room temperature. As observed by transmission electron microscopy (TEM),[5] this large lattice mismatch is overcome by a wall of sessile dislocations (Burgers vectors parallel to the substrate and having a Schmid factor equal to zero) lying in the CaF_2/BaF_2 interface with dislocation lines spaced approximately every seventh layer. Although CaF_2, BaF_2, and PbSe have well-matched thermal-expansion coefficients ($\sim 19\times 10^{-6}$/K), the difference of the thermal expansion coefficients between the $PbSe/BaF_2/CaF_2$ heterostructure and the Si substrate is as large as 700% at room temperature. Using scanning tunneling microscopy (STM), Zogg *et al.*[11] observed thermal-mismatch strain relaxations in $PbSe/CaF_2/BaF_2$ grown on Si(111) substrates by glide of dislocations in the primary $\{100\}\langle 110\rangle$ glide system. In this section, the dislocation slip resulting from the relaxation of thermal mismatch strain in PbSe epilayers observed at the growth interface by optical Normarski microscopy is described for the first time.

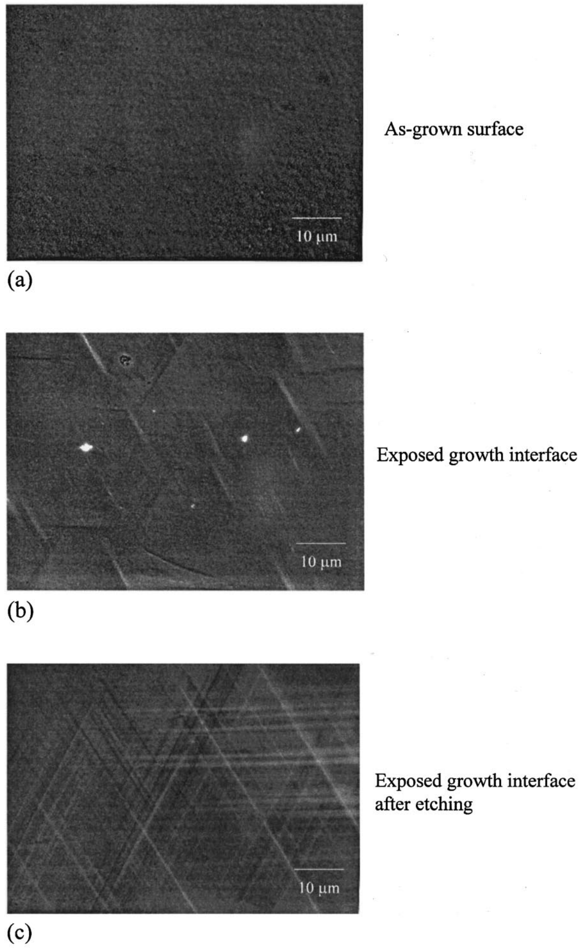

FIG. 3. Straight slip lines on a PbSe epilayer, for as-grown $PbSe/BaF_2/CaF_2$ on Si(111) (a), exposed $PbSe/BaF_2$ growth interface (b), and exposed $PbSe/BaF_2$ growth interface after slight etching (c). Each line is made up of a large number of slip steps on closely spaced parallel slip planes. The most prominent features in (c) are three sets of parallel straight steps with 60° angles between each set.

Figure 3 shows optical Nomarski microscopy micrographs of PbSe layers grown in this study. Figure 3(a) displays the morphology of an as-grown PbSe surface. It is seen that the surface is smooth and free of cracks. Some surface step lines oriented along the [110] direction are observed, which belongs to one of the threefold symmetric glide directions.[11,12] Figure 3(b) shows the morphology of an exposed $PbSe/BaF_2$ growth interface after PbSe epilayer transfer. Three groups of straight lines can be seen. These lines run along the three equivalent $\langle 110\rangle$ directions, the intercept of the glide planes with the surface. However, the density of lines is low (~770/cm). Figure 3(c) shows the morphology after the exposed PbSe growth interface was slightly etching using solution which consisted of HBr (95%) and 5% Br. A higher density (~2200/cm) of the straight slip lines (with threefold symmetry) running along the intersection of the {100} glide planes inclined by 54.7° with respect to the (111) layer surface were revealed. Their Burgers vectors are of the $1/2a\langle 110\rangle$ type. The application of the same Br/HBr etching solution to the surface of as-grown samples did not reveal any additional features indicating a much lower dislocation density at the top of the 3-μm-thick PbSe layer.

Compared with the morphology of the as-grown sample shown in Fig. 3(a), Fig. 3(c) shows two striking features. First, straight lines run along three equivalent $\langle 110\rangle$ directions, not only the [110] direction as shown in Fig. 3(a). Second, the length of lines extended from a few micrometers to about 100 μm. These features can result from the relaxation of thermal-expansion-mismatch strain because the support material (In–Au alloy) for the transferred PbSe is much softer than the Si substrate. After the removal of the CaF_2/BaF_2 buffer and the Si substrate, the thermal-mismatch strain in the PbSe layer was expected to be almost completely relaxed for all orientations. The change in local shear stress resulted in the rapid glide of existing threading segments of the misfit dislocations. When this moving segment glides and meets another threading segment they interact and join together, forming a longer misfit dislocation. Repetition of this process results in the formation of a long dislocation line, and thus, a long straight slip line. This process is different from the temperature cycles in which even after more than 1400 temperature cycles, plastic strain relaxation still occurs on each temperature change,[11] i.e., strain is still not totally relaxed.

IV. SUMMARY

High-quality PbSe thin films were heteroepitaxially grown by MBE on (111)-oriented silicon substrates. Successful transfer of 3-μm-thick PbSe epitaxial layers was accomplished by bonding the MBE-grown wafers face down to polished copper plates followed by the removal of the silicon growth substrate by dissolving the BaF_2 buffer layer in water. Surface profile characterization showed that the morphology of the bonded PbSe grown interface is smooth and comparable to the surface of the as-grown layer. High-resolution x-ray diffraction measurements demonstrated the complete removal of the BaF_2/CaF_2 buffer layer and the Si substrate and the high-crystalline quality of the transferred PbSe epilayer. Lattice-misfit dislocations and the relaxation of thermal-expansion-mismatch strain at the PbSe growth interface were observed for the first time by optical Nomarski microscopy. As a result, three sets of parallel straight slip lines with 60° angles between each set were revealed by slight etching of the growth interface. These high-density straight slip lines run along the intersection of the {100} glide planes inclined by 54.7° with respect to the (111) layer surface. Their Burgers vectors are of the $1/2a\langle 110\rangle$ type. Each line is made up of a large number of slip steps on closely spaced parallel slip planes. Such features are evidence of the large thermal-expansion-mismatch strain that occurred in the $PbSe/BaF_2/CaF_2$ layers.

In addition, we note that although the technologies involved in this work, such as epitaxy of PbSe using fluoride buffers, bonding, and lift-off, were developed on inexpensive Si substrates, they can be applied as well to lattice-mismatch and thermal-expansion-matched BaF_2 or IV–VI substrates such as PbSe.

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