Molecular beam epitaxy of periodic BaF_2/PbEuSe layers on Si(111)

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Bragg reflector structures consisting of BaF_2/PbEuSe stacks have been epitaxially grown on CaF_2/Si (111) substrates. The reflectors are centered at a wavelength of 4.0 μm with a bandwidth of about 3.0 μm. Reflectivity as high as 95% at the center wavelength has been achieved in three-stack reflectors. Cracks were visible under an optical Normarski microscope in two-stack reflectors. The formation of cracks is probably due to the accumulation of the residual thermal strain in thick layers or the hindrance of dislocation glide at the BaF_2/PbEuSe interfaces. © *1999 American Vacuum Society.* [S0734-211X(99)06203-4]

I. INTRODUCTION

Epitaxial growth of multilayer structures of alternating high and low refractive index materials with the optical thickness of each layer a quarter wavelength at the required wavelength have many applications as bandpass filters and distributed Bragg reflectors (DBRs). The difference in the refractive indices of constituent layers determines the reflectance bandwidth of a reflector and the number of stacks in the reflector necessary for achieving desired reflectivity at a center wavelength. If the refractive index ratio is low as in GaAs/AlGaAs heterostructures, a large number of layers of exactly the same optical thickness are required to achieve high reflectivity. For fabrication of Bragg reflectors with center wavelengths in the range of 1.3–5.0 μm, it is desirable to grow heterostructures with high refractive index ratio. One materials system is the IIa-fluoride/AlGaAs pair grown by molecular beam epitaxy (MBE) on GaAs.[1,2] Because of the low refractive index of IIa-fluorides (about 1.45) with respect to that of GaAs (3.59), high reflectance and broad bandwidth of the quarter-wavelength DBRs consisting of only three stacks of (CaF_2–BaF_2–CaF_2) and GaAs have been achieved at the center wavelength of 1.4 μm.[2]

IIa-fluoride/PbEuSe is another materials combination with an even higher refractive index ratio. PbEuSe is a ternary IV–VI semiconductor with a NaCl crystal structure. With Eu content of 0.8%, the refractive index of PbEuSe is as high as 4.65.[3] Theoretical calculations indicate that reflectivity as high as 99.9% can be obtained in a three-stack BaF_2/PbEuSe Bragg reflector at a central wavelength of 4.0 μm with a reflectance bandwidth of 3.0 μm. Therefore, IIa-fluoride/PbEuSe Bragg reflectors have potential applications as optoelectronic components in making mid-infrared vertical cavity surface emitting devices.

Both BaF_2 and PbEuSe can be epitaxially grown on Si (111).[4,5] Using silicon as a substrate takes advantage of its low cost and large wafer size. Though BaF_2 and PbEuSE have similar lattice constants and thermal expansion coefficients, they are lattice and thermal mismatched with Si. For example, at room temperature the lattice mismatch between Si and BaF_2 is about 14.2%, while the thermal expansion coefficient of Si is about seven times lower than that of BaF_2. However, previous studies indicate that the thermal strain built up on cooling from growth temperature to room temperature is substantially relieved through dislocation glide in certain slip planes, resulting in crack-free epilayers for typical thicknesses of 200 nm for BaF_2 and 2 μm for PbSe.[4] For a BaF_2/PbEuSe Bragg reflector with a center wavelength of 4 μm, the thicknesses of each quarter-wavelength BaF_2 and PbEuSe layer are 690 and 220 nm, respectively. As the number of stacks in a BaF_2/PbEuSe multilayer structure increases, the total thickness of the BaF_2 and PbEuSe layers will increase linearly. There have been no reports on the extent of BaF_2 layer thickness at which the thermal strain is relieved through the formation of cracks.

In this work, BaF_2/PbEuSe Bragg reflector structures are grown on CaF_2/Si (111) by MBE. Using BaF_2 instead of CaF_2 as one of the constituent quarter-wavelength layers allows the thermal strain to be relieved more effectively because BaF_2 has lower elastic constants than CaF_2. Other reasons for using BaF_2 are that it has a higher growth rate than CaF_2 and has a better lattice match with PbEuSe. In order to reduce the thermal mismatch strain, the BaF_2 layers were grown at 320 °C, well below the normal BaF_2 growth temperatures of 500–700 °C. This article shows that BaF_2 and PbEuSe can be epitaxially grown onto each other with good crystalline quality. A reflection band centered at 4.0 μm with a bandwidth of about 3.0 μm has been obtained in Bragg reflectors with three BaF_2/PbEuSe stacks. The reflectivity near the center wavelength is as high as 95%.

II. MBE GROWTH PROCEDURES

The growth of BaF_2 and PbEuSe layers on Si (111) was carried out in an Intevac Modular GEN II MBE system. 3 in. diameter p^+-type (0.005–0.025 Ω cm) Si (111) wafers with

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offcut angles less than 0.3° were cleaned using a modified Shiraki method followed by dipping in a HF solution. Si wafers were outgassed in the buffer chamber at 200 °C for 1 h before loaded into the growth chamber. Auger spectroscopy analysis was performed on thermally cleaned Si (111) wafers. No carbon related Auger peaks were observed after the hydrogen-passivated layer was desorbed from the Si surface at the temperatures of 540 °C.

Before growing BaF_2 and PbEuSe, a 2-nm-thick CaF_2 was first deposited on a thermally cleaned Si substrate at 700 °C. Both CaF_2 and BaF_2 growths were accomplished by heating high-purity polycrystalline CaF_2 and BaF_2 in dual zone effusion cells. The BaF_2 growth rate, calibrated by measuring the BaF_2 layer thickness using an ellipsometer and a Tencor step scan profiler, was about 4 nm/min at the cell temperature of 1165 °C.

PbEuSe growth was accomplished by evaporating the bulk PbSe and elemental Eu from low-temperature effusion cells. An additional Se source was used to control the stoichiometry of the PbEuSe layers and keep the surface under Se rich conditions. An EPI valved cracker was used to produce a Se flux of 10% relative to the PbSe flux in the growth of PbEuSe with 3% Eu content. The PbEuSe growth rate was about 0.8 μm/h.

Good crystalline quality of the BaF_2 layers grown on Si (111) can be obtained in a wide growth temperature range of 400–700 °C.[6] In this work, the growth of BaF_2 layers was not carried out in the optimum temperature range but rather at the temperature of 320 °C. This low-temperature growth is expected to reduce the thermal mismatch strain in the BaF_2 layers and the desorption of Se from the PbEuSe layers as well. All the PbEuSe layers were grown at a temperature of 300 °C. In the growth of the first stack, the BaF_2 layer was first deposited on the CaF_2/Si (111) substrate followed by the growth of the PbEuSe layer. The growth of more stacks followed the same sequence.

The optical thicknesses of the BaF_2 and PbEuSe layers were calculated using the expression $d=\lambda/(4n)$, where λ is the center wavelength of the reflector and n is the refractive index of each layer. Refractive indices of 1.45 for BaF_2 and 4.65 for PbEuSe were used in the calculations. For a reflector with a center wavelength of 4.0 μm, the corresponding optical thicknesses of the BaF_2 and PbEuSe layers are 690 and 220 nm, respectively. Since the center wavelength of Bragg reflectors is designed at 4.0 μm, it is necessary to reduce absorption in the wavelength range of 2.5–5.5 μm. With 3% Eu used in growing PbEuSe, the room temperature absorption edge of PbEuSe is expected to be near 3.0 μm,[7] close to the short wavelength edge of the reflector.

Growth was *in situ* monitored using the reflection high-energy electron diffraction (RHEED) technique. The structural characterization of the layers was performed using a Philips high resolution x-ray diffraction system with a four-crystal Ge (220) monochromator. An optical Normarski microscope was used to examine the surface morphology of the as-grown films. In the reflectance measurements, the monochromatic incident light was produced using a black body and a monochromator. The reflected light was detected using a mercury cadmium telluride detector. Both incident and reflected lights were at an angle of 45° relative to the surface normal. After the reflectance data were collected, a calibration was made by taking into account the oblique incidence geometry.

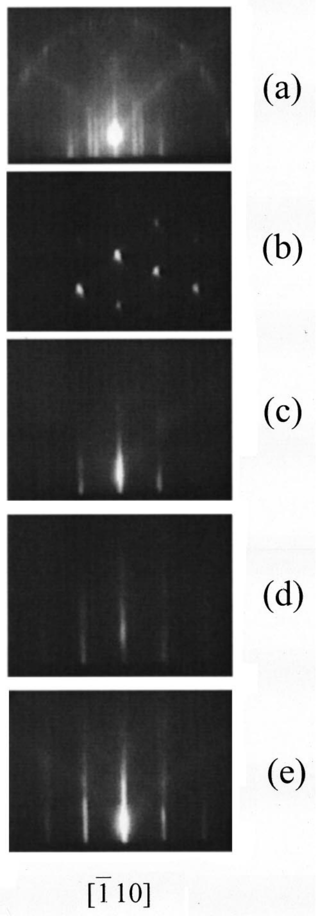

FIG. 1. RHEED patterns recorded at the [$\bar{1}$10] azimuth: (a) Si (7×7) after desorption of a hydrogen-terminated passive layer; (b) the initial growth of PbEuSe on BaF_2 with a coverage of 0.4 nm; (c) the growth of PbEuSe on BaF_2 with a coverage of 130 nm; (d) the initial growth of BaF_2 on PbEuSe with a coverage of 0.7 nm; and (e) the growth of BaF_2 on PbEuSe with a coverage of 670 nm.

III. RESULTS AND DISCUSSION

At the initial stage, the growth of PbEuSe on BaF_2 proceeds via a three-dimensional (3D) Volmer–Weber growth mode due to the higher (111) free surface energy of PbEuSe as compared to BaF_2. This is evidenced by the appearance of transmission electron diffraction spots on RHEED patterns as shown in Fig. 1(b). As the PbEuSe coverage increases to approximately 10 nm, the diffraction spots were gradually replaced by (1×1) streaks, indicating that the surface islands start to coalescence and a continuous layer is formed. Figure 1(c) shows a RHEED pattern for a 130-nm-thick PbEuSe.

The growth of BaF_2 on PbEuSe is expected to proceed via a two-dimensional (2D) Franck–van-de-Merwe growth mode because it is an opposite process relative to the growth

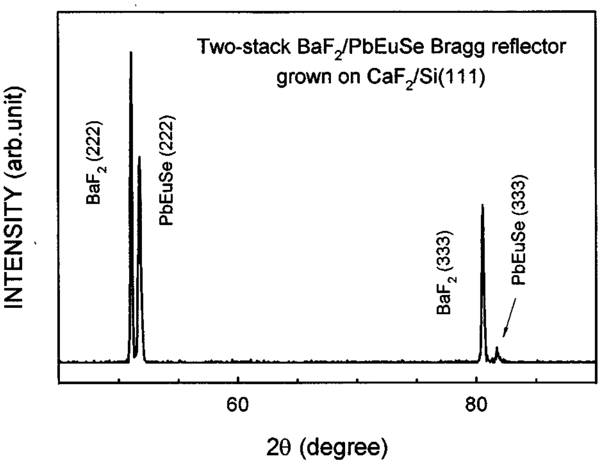

FIG. 2. XRD rocking curve for a Bragg reflector with two BaF_2/PbEuSe stacks.

of PbEuSe on BaF_2. Figure 1(d) shows that the diffraction pattern remains streaky at the initial stage of the BaF_2 growth. Note that as the BaF_2 flux starts to impinge on the PbEuSe surface, there is a decrease in the diffraction streak intensity. It was also observed that after the BaF_2 coverage increases to a few monolayers (3.58 Å thick for one monolayer), the diffraction streaks were changed into dashed-line streaks. After about one period of time for one monolayer growth, the straight streaks appeared again. This implies that during the initial growth of BaF_2 on PbEuSe, there may still be a certain degree of surface roughness present on the surface. As the BaF_2 coverage continues, the surface becomes smooth as indicated by the appearance of the Kikuchi lines and the bright streaky diffraction lines shown in Fig. 1(e).

In the growth of the reflector structures, both BaF_2 and PbEuSe layers keep the same (111) orientation as the Si substrate. Figure 2 is a typical x-ray diffraction (XRD) rocking curve for a BaF_2/PbEuSe reflector with two stacks. Since the CaF_2 buffer layer was grown at 700 °C, the epitaxial relationship of the CaF_2 layer relative to the Si substrate is type B,[6] that is, the lattice of the CaF_2 layer is rotated by 180° with respect to the Si substrate. The first BaF_2 layer grown at 320 °C has the same epitaxial relationship as the underlying CaF_2 layer with respect to the Si substrate. X-ray data also confirmed that the epitaxial relationship between BaF_2 and PbEuSe layers is always type B as previously reported.[8] This is because for a stacking sequence where the PbEuSe layer is rotated by 180°, the Ba–Se and the F–Pb (or F–Eu) bond distances that the interface are minimized, whereas the energetically unfavorable Ba–Pb and F–Se bond distances are maximized.[8,9]

Figure 3 shows optical Normarski pictures of the PbEuSe surface morphologies of Bragg reflectors with one, two, and three stacks of BaF_2/PbEuSe. For the Bragg reflector with one BaF_2/PbEuSe stack, the film exhibits no cracks. For the reflector with two BaF_2/PbEuSe stacks, however, a few cracks are visible under the optical Normarski microscope. It was observed that most of the crack lines are associated with some kind of surface defects, that is, they either pass through the defects or terminate at the defects as shown in Fig. 3(b). This is probably indicative of localized stress, which seems to be centered at the point of nucleation of the crack.[10] For the reflector with three BaF_2/PbEuSe stacks, the film exhibits a network of cracks [Fig. 3(c)]. The cracks are along [−110], [10−1], and [0−11] directions.

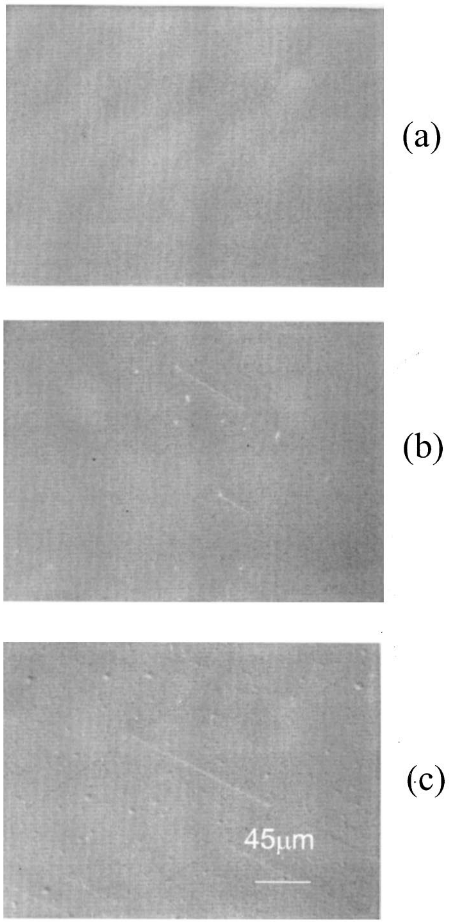

FIG. 3. Optical Normarski microscopy view of the surface morphology of Bragg reflectors with one, two, and three stacks of BaF_2/PbEuSe.

It is known that the thermal mismatch strain in stacks of PbSe, BaF_2, and/or CaF_2 on Si (111) substrates is relieved by the glide of dislocations in the principal ⟨110⟩ {100} glide system.[4] Dislocations with Burgers vectors inclined to the surface may nucleate at the surface, become misfit dislocations after glide to the interface, and leave a surface step behind. Even though it has been demonstrated that the overgrowth of PbSe does not affect the strain state of the underlying BaF_2,[4] it is still probable that the strain-relieving dislocation glide may stop at the BaF_2/PbEuSe interface since PbEuSe and BaF_2 grow type B with respect to each other and therefore the gliding planes in BaF_2 layers are not aligned with the ones in PbEuSe layers, which may reduce the plastic deformation necessary for the thermal strain relaxation. If this is the case, the dislocation glide would become more difficult as the number of BaF_2/PbEuSe interfaces increases. This might partially explain the increase of the crack density with increasing the number of the BaF_2/PbEuSe stacks. The

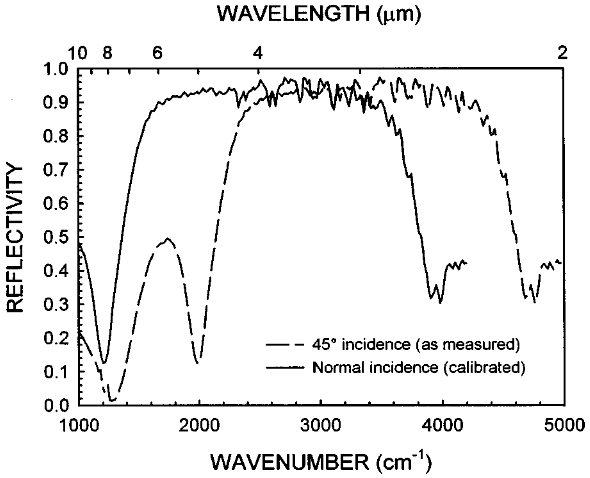

FIG. 4. Reflectance spectra obtained from a Bragg reflector with three BaF_2/PbEuSe stacks. The curve with solid line corresponds to normal incidence (calibrated) while the curve with dashed line corresponds to 45° incidence (as measured).

cracks observed in this study have the same directions as the slip lines originated from the surface steps. Since the cleavage planes of BaF_2 and PbSe are {111} and {100}, respectively, it is likely that the cracks are nucleated in the BaF_2 layers and extended to the surface along its cleavage planes. This indicates that the formation of cracks provides another channel to relieve the thermal strain.

It has also been reported that the strain in the BaF_2 and PbSe layers grown on CaF_2/Si (111) relaxes approximately proportionally to $1/d$ where d is the thickness of the corresponding layer, but the absolute values predicted by Mathew's theory are much lower.[4] This slow residual strain relaxation is attributed to some kind of pronounced friction forces. According to Matthew's theory,[11] the strain energy in a layer is also proportional to the layer thickness. Therefore, the slow residual strain relaxation may increase the accumulation of the thermal strain as the total thickness of the film increases. This is especially true for BaF_2 overgrowth because the BaF_2 layers are much thicker than the PbEuSe layers and BaF_2 has higher elastic constants, which makes the dislocation glide in the BaF_2 layers not as easy as in the PbSe layers. It is not clear whether the formation of the cracks starts in the BaF_2 layer or the PbEuSe layer. As previously reported,[4] for PbSe layers grown on BaF_2/CaF_2/Si (111) with thicknesses less than 1.0 μm, the measured rhombohedral distortion is in the range of 2%–8%. Since the thickness of the PbEuSe in a BaF_2/PbEuSe Bragg reflector with the center wavelength of 4 μm is about 0.22 μm, the thermal strain accumulated in the PbEuSe layers may also be responsible for creation of the cracks.

Figure 4 shows reflectance spectra for a Bragg reflector with three BaF_2/PbEuSe stacks. The dashed line curve is the original spectrum taken in an oblique incident geometry. The solid line curve is the spectrum corresponding to a normal incidence geometry obtained after calibration. It is seen from the calibrated spectrum that the actual center wavelength of the reflector is close to the designed value. The bandwidth with reflectance above 90% is about 3.0 μm.

IV. CONCLUSION

Bragg reflectors consisting of BaF_2 and PbEuSe layers have been epitaxially grown on Si (111) substrates. The initial growth of PbEuSe on BaF_2 proceeds via a Volmer–Weber 3D growth mode while for BaF_2 on PbEuSe the growth proceeds via a 2D Frank–van-der-Merwe growth mode from the very beginning. Broad bandwidth (~3 μm) reflectors with reflectivity of 95% at a center wavelength of 4.0 μm for normally incident light have been obtained with three BaF_2/PbEuSe stacks. These Bragg reflectors may find important applications in making vertical cavity surface emitting devices. Cracks start to form on the surface of the two-stack reflectors as a result of relieving the residual thermal strain. Further improvement in the characteristics of these reflectors is possible if the BaF_2 layers are grown at lower temperatures or the reflector structures are grown on lattice and thermal matched BaF_2 substrates.

ACKNOWLEDGMENT

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