HOT WALL BEAM EPITAXIAL GROWTH OF PbTe LAYERS ON $BaF_2/CaF_2/Si(111)$ SUBSTRATES

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ABSTRACT

PbTe(111) thin films were grown by the hot wall beam epitaxy (HWBE) technique on Si(111) substrates using intermediate BaF_2/CaF_2 buffers grown by MBE. The best PbTe layers exhibit the high resolution X-ray rocking curve linewidth of about 130 arcsec, the low temperature Hall mobility of 8×10^5 cm^2/Vs, and an excellent surface morphology with the roughness of a few angstrom as it was determined by the atomic force microscopy (AFM). The results indicate that high-quality PbTe films can be obtained on fluoride covered Si(111) substrates by simple and cheap HWBE method.

1. INTRODUCTION

Lead chalcogenide (IV-VI) narrow gap semiconductors are well known infrared (IR) materials suitable for photodetector [1] and laser [2] applications. Their growth on Si substrates opens up a unique possibility for a new generation of IR focal plane arrays monolithically integrated with read-out Si-electronics. Besides, the substitution of traditional substrate materials such as IV-VI and BaF_2 bulk crystals by Si wafers allows one to increase output power of lead salt IR lasers due to well above thermoconductivity of silicon.

Despite the very high lattice (~19% for PbTe) and thermal expansion coefficient mismatch (~8 times large for PbTe) the IV-VI compounds can be grown on Si(111) using fluoride layers (BaF_2/CaF_2 or CaF_2 only) as a intermediate buffer [3].

For a fluoride epitaxy it is necessary to use the MBE technique only, but for lead chalcogenides the HWBE technique can be successfully used too [4]. Moreover, HWBE has a certain advantage to obtain the PbTe films offered more low concentrations of free carriers. While PbTe sublimes congruently by molecules and it is usually evaporated from a compound source, due to resublimation of the PbTe source material within the effusion cell, the composition of the emitted flux can deviate significantly from exact stoichiometry [5]. Since the source temperatures in HWBE are well lower than those in MBE method, the maintenance of stoichiometric beam flux composition and, hence, the preparation of films with the low carrier concentration can be significantly easy achieved by HWBE method.

We have reported about HWBE growth of PbTe films with electron concentrations below 10^{17} cm^{-3} on fluoride covered Si substrates [6,7], but the crystal quality of those films was still behind of the best IV-VI layers obtained by MBE technique [8-10]. In this paper, the recent results on optimized HWBE growth of PbTe films are described. They demonstrate that PbTe can be grown on Si(111) by the simple and cheap HWBE technique with the same high crystal quality as ones obtained by MBE.

2. EXPERIMENTS

The fluoride buffer layers were grown in a custom built MBE apparatus on Si(111) wafers using resistively heated crucibles. The substrates were cleaned using a final dipping into HF-solution to ensure hydrogen-passivated surface. The details of a stacked BaF_2-CaF_2 buffer growth have been described elsewhere [6,7]. Briefly, after a substrate preheating up to 800°C a thin CaF_2 layer with a thickness below the critical thickness for misfit dislocation creation (20Å at the growth temperature of 750°C) was firstly grown, immediately followed by deposition of about 1200Å of BaF_2 layer. The growth rate of both fluorides was

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adjusted to about 1Å/s. The as-grown samples were stored in dry air and then loaded into a second deposition apparatus designed for deposition by HWBE method. This system is consisted of a preheating stage and a PbTe reactor, which is equipped with an additional Te sources serving for a fine-tuning of the carrier concentration. The preheating stage is also supplied with another Te source for the pretreatment of fluoride surface in Te_2 flux to obtain a Te-terminated BaF_2(111) surface[11]. Prior to the PbTe growth, the substrates were annealed under the Te_2 flux at temperatures of 400-500°C and then transferred from the preheating oven to the PbTe reactor. Then the PbTe films were grown at substrate temperature of 380-400°C with the rate of 3.5-4.0Å/s (~1 monolayer/s).

The growth of fluorides was monitored by *in situ* reflection high-energy electron diffraction (RHEED). The thickness of fluoride layers was defined by optical ellipsometry, whereas for determination of PbTe films thickness the Fourier transform IR transmission method was used. The surface morphology of fluoride and PbTe layers was investigated by AFM on the different stages of epitaxy. The crystal quality of PbTe films was defined by the rocking curve measurements using a double-crystal X-ray spectrometer. The carrier concentration and mobility were determined from Hall measurements at temperatures from 11 to 300K by the Van der Pauw method.

3. RESULTS AND DISCUSSION

During all stages of fluoride growth from the beginning CaF_2 nucleation to the completing BaF_2 deposition, the only streaked RHEED patterns without any spots were observed. That points to an atomically flat surface of fluorides and a layer-by-layer (2D) growth mode at the <111>-growth direction. The 2D growth in spite of very high lattice mismatch (~14% between BaF_2 and Si) is attributed to extremely low free energy of the (111) fluoride surfaces [12].

However, the very low free energy of natural fluoride terminated BaF_2 (111) surface prevents 2D nucleation (which is desired) of PbTe on BaF_2/CaF_2/Si(111) substrates, despite of the much less lattice mismatch between PbTe and BaF_2 (~4%). So the PbTe tends to nucleate in a island (3D) growth mode to maintain the minimum energy configuration of the system. To improve nucleation of PbTe on BaF_2(111) surface, the preliminary procedure of substrate annealing under Te_2 flux was employed before the beginning of PbTe growth. This treatment leads probably to formation of Te-terminated surface of BaF_2(111) [11]. Figure 1 shows the initial stage (before a coalescence of islands) of PbTe nucleation on the Te-treatment surface of BaF_2. The triangles which can be seen on Fig.1(a) are due to triangular steps on BaF_2 surface originating at cool down from growth temperature as a result of the high thermal expansion coefficient mismatch between Si and fluoride [10].

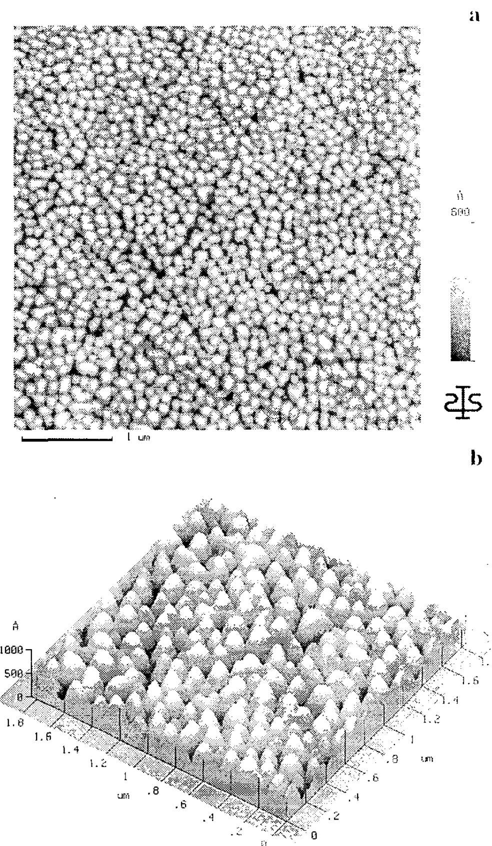

Fig. 1. AFM images of PbTe islands grown at 400°C on BaF_2/CaF_2/Si(111) substrate with equivalent film thickness of ~250Å:(a) 4.6×4.6μm, (b) 1.85×1.85μm image size.

It is clear that for HWBE as well for MBE the growth of PbTe on BaF_2(111) starts with 3D growth mode by formation of large pyramidal

islands around the cores of threading dislocations[5]. This mechanism of nucleation is unaffected by the steps presented on BaF_2 surface. At growth temperature of 400°C the transformation from 3D to 2D growth are occurred at ~1000Å thickness of PbTe layer. It has been reported that for MBE at 350°C such transformation takes place on the thickness of ~2000Å [5]. The origin of the significant reduction in the thickness of highly defected transient layer can be probably attributed in our case to more homogeneous nucleation of PbTe islands owing to the formation of Te-terminated BaF_2 surface [11].

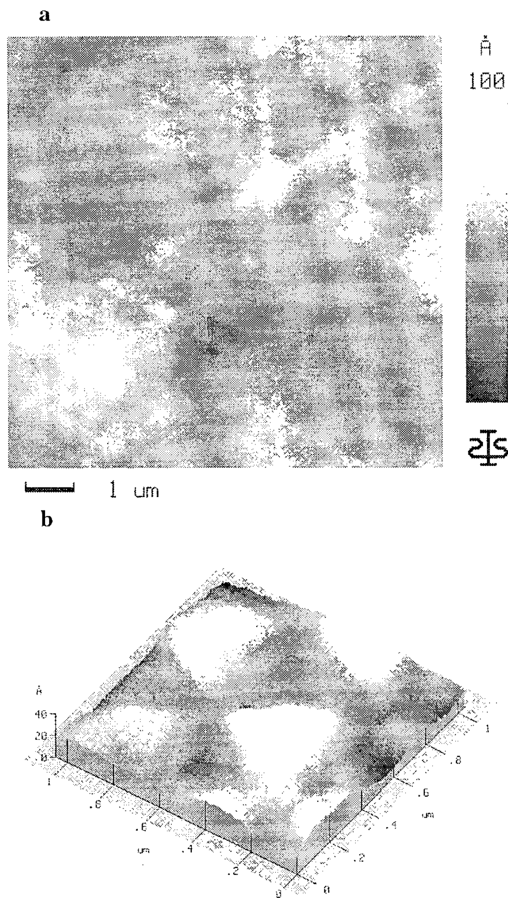

Fig. 2. AFM images of a PbTe layer (3.1μm thick) grown on $BaF_2/CaF_2/Si(111)$ at 400°C: (a) 9.1×9.1 μm, (b) 1.05×1.05μm image size.

The thick PbTe layers grown on the $BaF_2/CaF_2/Si(111)$ ensure a very smooth surface, in spite of the initial 3D nucleation. The surface morphology of PbTe layer with a thickness of about 3.1μm is shown on Fig. 2. The three sets of straight lines are parallel to three ⟨011⟩ surface directions. These steps result from the thermal strain relaxation during cool down from growth to room temperature (RT) [10]. The root mean square (RMS) value of roughness is equal to 12.76Å for PbTe surface shown on Fig. 2(a) and 5.41Å for smaller size of AFM image on Fig.2(b). For comparison, the RMS of roughness is equal to 121.6Å and 121.0Å for surfaces shown on Fig.1(a) and (b) respectively.

The epitaxial relation between PbTe and Si was determined by comparison of X-ray reflection directions from the inclined (311) planes of film and substrate. This asymmetric X-ray diffraction data indicated an untwined PbTe films with a lattice orientation identical to that of Si substrate. Since the fluoride buffer grows with its lattice rotated by 180° around the surface normal [3], the PbTe has grown also with the same 180° rotation regarding to the underlying BaF_2. The double crystal X-ray rocking curve shown in Fig. 3, confirm that the thick PbTe films are high quality single crystals. The full width at half-maximum (FWHM) of the PbTe(333) diffraction peak was as low as 130 arcsec. This value of FWHM is not distinguished from the values obtained on the best IV-VI films grown on Si by MBE [8,10].

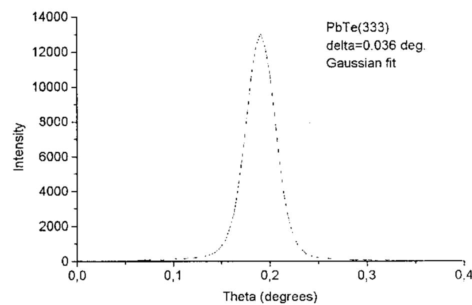

Fig. 3. X-ray double crystal rocking curve the (333) diffraction peak with FWHM=130 arcsec of PbTe layer with a thickness of 3.1μm grown at 400°C on $BaF_2/CaF_2/Si(111)$.

Since the low temperature (<15K) carrier mobility of lead chalcogeniges is limited by structural defects such as threading dislocations [13], the Hall

measurements of electrical properties were also employed for evaluation of PbTe crystal quality. The best n-type PbTe films with the low temperature electron concentrations between 4×10^{16} and $9\times10^{16}cm^{-3}$ have values of the electron mobility as high as 8×10^{5} cm^2/Vs at 11K (the lowest temperature in used installation). This value even exceeds the best reported mobilities for PbTe grown on Si by MBE, but is still some behind of those grown on $BaF_2(111)$ bulk crystal [5].

For application of PbTe/fluoride/Si structures it is necessary to obtain a full relaxation of strains arising due to high mismatch of thermal expansion coefficients between PbTe and Si, since the IR photodetectors and lasers are operated at cryogenic temperatures but stored at RT. To estimate the ability for the strain relaxation, the several thermocycles between RT and 77K was made by direct dipping of grown samples into liquid nitrogen and warming it rapidly back to RT. The AFM, X-ray diffraction and Hall measurements were carried out after such thermocycling. They are shown that the high quality samples are exhibited an excellent ability for the relaxation of thermal strains. The values of the rocking curve FWHM, and the low temperature mobility were left almost constant, and only additional surface steps were revealed on PbTe surface. It is such PbTe surface, which has shown on Fig. 2. The revealing of additional steps after the thermocycling allows one to conclude that PbTe layers are capable of relieving most of the thermal mismatch strain even cryogenic temperatures by plasticity mechanism described previously [10].

4. CONCLUSIONS

It has been demonstrated the effectiveness of HWBE technique for epitaxy of high quality PbTe films on Si(111) substrates with fluoride buffer. The principal properties of the films such as crystal structure, surface morphology, carrier mobility, and ability for the thermal stress relaxation are just as good as those of PbTe films obtained by MBE.

ACKNOWLEGEMENTS

This research has been supported in part by INTAS project 96-0535. The author is indebted to Prof. Th.Schimmel and Dr. P.Schunk (Universität Karlsruhe, Germany) for AFM investigations and to Dr. A.G.Fedorov (Inst. for Single Crystals, Kharkov, Ukraine) for X-ray measurements.

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