

Characterization of PbTe Epitaxial Layers Grown on BaF₂/CaF₂/Si Structures

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In this paper we present a characterization of PbTe epilayers grown by hot wall epitaxy on silicon using II-a fluorides as intermediate layers. The PbTe layers were characterized electrically by temperature dependent Hall effect measurements. A detailed study of the strain in CaF₂ layers grown on Si(111) substrates was performed by high resolution x-ray diffraction analysis. To simulate the real operation conditions of the lead chalcogenides infrared devices, the CaF₂/Si structure was submitted to thermal cycles from 300 to 77K and a ω scan was measured after each cycle.

I. Introduction

The interest in the epitaxy of lead chalcogenides on silicon has recently increased due to the possibility of fabricating IV-VI semiconductor compounds infrared devices integrated monolithically to the Si substrate. Since the epitaxial growth of narrow gap lead chalcogenides directly on Si presents problems due to the large differences in lattice constants and thermal expansion coefficients, researches have been carried out on the possibility to interpose II-a fluoride buffer layers between the two semiconductor materials^[1,2,3].

In the IV-VI compounds epitaxy on Si substrates, CaF₂ is normally chosen as the first buffer layer because of the small lattice mismatch relative to Si (0.5% at room temperature) followed by a BaF₂ layer which has a close match of lattice constant and thermal expansion coefficient to the lead chalcogenides ones. Although the CaF₂ lattice constant (5.46Å) is very close to Si (5.43Å), the large difference in thermal expansion coefficients between CaF₂ ($19.2 \times 10^{-6} \text{ K}^{-1}$) and Si ($2.6 \times 10^{-6} \text{ K}^{-1}$) imposes some limits in the epitaxial growth^[4,5]. In order to obtain good monocrystalline lead chalcogenides epilayers on

the BaF₂/CaF₂/Si structure, the strain relief mechanisms of the thermal mismatch in the CaF₂/Si system must be well understood.

In this work we report on the electrical and structural characterization of PbTe layers grown by hot wall epitaxy technique on BaF₂/(CaF₂/Si structure, as well as a detailed analysis of the strain situation in the CaF₂/Si system by high resolution x-ray diffraction measurements. To simulate the real condition of the operation of the infrared detectors, the CaF₂/Si system was submitted to thermal cycles from room to liquid nitrogen temperature and the x-ray rocking curves were measured after each thermal cycle.

II. Experimental procedure

The films were grown in a home made hot wall epitaxy (HWE) system^[3] consisted of a high vacuum chamber with two HWE reactors for the lead telluride compounds, each one with an additional Te compensation source, and two graphite effusion cells for the fluorides. The background pressure during growth was 10^{-7} mbar. The Si substrate is placed inside a furnace that fits on top of a rotator disc, that allows the

growth of several layers without vacuum breaking. Due to the preferential (111) growth of the fluorides, Si(111) substrates were used. Details about the growth procedure were published elsewhere^[3]. To measure the layer thickness perfilemetry and ellipsometry methods were used for the fluoride layers and interferometry for the PbTe ones.

III. Electrical properties

To characterize the PbTe layer electrically Hall effect and resistivity measurements were made from room temperature down to 13K in an automatic temperature dependent Hall effect system using the Van der Pauw geometry.

The electrical properties of the PbTe layers grown on top of the BaF₂/CaF₂/Si structures were compared with PbTe layers grown directly on BaF₂(111) substrate. Fig. 1 shows the Hall mobility as a function of temperature for a typical p-type PbTe layer ($1.5 \times 10^{17} \text{cm}^{-3}$) grown on BaF₂/CaF₂/Si structure and for a PbTe layer with the same carrier type and concentration grown directly on a BaF₂ substrate. For the layer PbTe/BaF₂, the mobility is limited at high temperatures by acoustic phonons ($\mu \sim T^{-5/2}$) while at low temperatures some defects (or impurities) limits the mobility at $3 \times 10^5 \text{cm}^2/\text{V.s}$. In case of PbTe/BaF₂/CaF₂/Si the amount of defects start to limit the mobility already at approximately 150K causing a deviation from the phonon limited curve ($\mu \sim T^{-5/2}$) and a saturation in the mobility at low temperatures at a value 10 times lower. These defects on the PbTe layer of the PbTe/BaF₂/CaF₂/Si structure are caused by dislocations created by the differences in lattice constants and thermal expansion coefficients between the semiconductor materials.

By adjusting very well the thicknesses of the fluoride buffer layers, specially by controlling the CaF₂ layer thickness not to exceed 10 nm and optimizing the growth parameters it was possible to obtain a n-type PbTe layer on top of the BaF₂/CaF₂/Si structure with mobility values of $5 \times 10^4 \text{cm}^2/\text{V.s}$ at 20K.

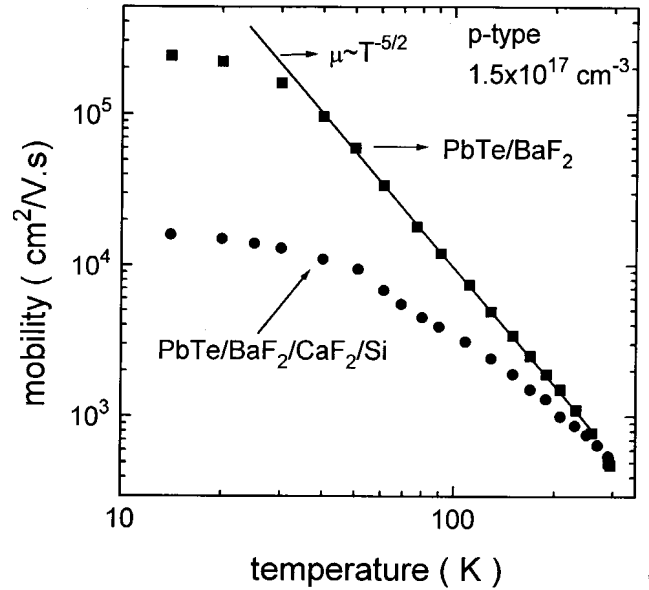


Figure 1. Hall mobility of PbTe layer as a function of temperature grown on BaF₂ substrate and on BaF₂/CaF₂/Si structure.

As the quality of the CaF₂ first buffer layer showed to be the most important in the whole structure, we decided to make a detailed study on the CaF₂/Si structure.

IV. High resolution X-ray diffraction measurements

In order to analyze the CaF₂/Si(111) structurally, x-ray diffraction techniques were used. In standard x-ray diffraction $\Theta/2\Theta$ scans, the CaF₂/Si(111) showed only the symmetrical Bragg diffraction peaks. It was not possible to distinguish the CaF₂ peaks under the Si ones using this technique. High resolution x-ray diffraction (HRXD) measurements were then performed using a two-crystal diffractometer with a GaAs crystal monochromator for the CuK α radiation with a final resolution of 17 arcsec.

Fig. 2 shows a ω scan of a (15 nm) CaF₂/Si structure where the CaF₂(333) Bragg peak appears as a shoulder near the Si(333) peak. For comparison the (333) peak of a Si substrate is also plotted in the figure. This position of the CaF₂(333) Bragg peak cannot be explained with a simple pseudomorphic growth model since in this case a compressive strain is expected due to the larger CaF₂ lattice constant relative to Si. The tensile strain in the plane of the CaF₂ layer can only be understood if the large difference in thermal expansion coefficients

between CaF_2 and Si is taken into account^[6,7]. This difference increases the lattice misfit between CaF_2 and Si from 0.5% at room temperature to 2.2% at growth temperature (730°C).

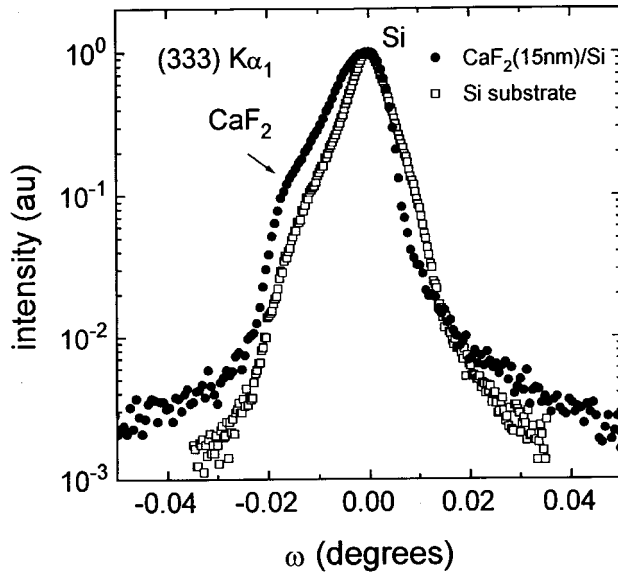


Figure 2. ω scan of the (333) Bragg reflection of the CaF_2/Si structure and of a Si substrate.

In order to calculate the angular separation $\Delta\omega$ between the $\text{CaF}_2(333)$ and the $\text{Si}(333)$ symmetrical Bragg peak, the elastic theory combined with Bragg diffraction law was used. The relation of the perpendicular (ϵ_{\perp}) to the parallel strain (ϵ_{\parallel}) taken from the elastic theory for a cubic crystal in the (111) direction assuming tetragonal distortion and using bulk elastic constants C_{ij} for the CaF_2 layer is:

$$\epsilon_{\perp} = -2 \left[\frac{(C_{11} + 2C_{12} - 2C_{44})}{(C_{11} + 2C_{22} + 4C_{44})} \right] \epsilon_{\parallel} = -1.01\epsilon_{\parallel}$$

In case of a pseudomorphic growth (compressive strain with $\epsilon_{\parallel} = -0.5\%$) the calculated angular separation is $\Delta\omega = -0.56^\circ$ or in case of a completely relaxed CaF_2 layer on Si at room temperature ($\epsilon_{\parallel} = 0$), $\Delta\omega = -0.28^\circ$.

In the proposed model, considering that the CaF_2 layer is completely relaxed at growth temperature where interfacial defects such as misfit dislocations accommodate the 2.2% lattice misfit, a tensile strain in the layer is built up during cooling down to room temperature due to the thermal mismatch. Assuming complete pinning of these defects (no atomic rearrangement) during cooling, the maximum tensile strain in the

layer is $\epsilon_{\parallel} = 1.7\%$. In this case we calculate $\Delta\omega = 0.81^\circ$. If the CaF_2 layer is assumed to be totally relaxed at growth temperature and R represents the degree of relaxation in % of the thermal strain during cooling (R=0 for maximum thermal strain $\epsilon_{\parallel} = 1.7\%$ and R=100 for $\epsilon_{\parallel} = 0$), a relaxation degree R=75% during cooling down process is necessary to fit the position of the measured $\text{CaF}_2(333)$ peak. This result agrees with the tetragonal distortion determined previously from RBS ion channeling measurements in CaF_2/Si system^[6,7].

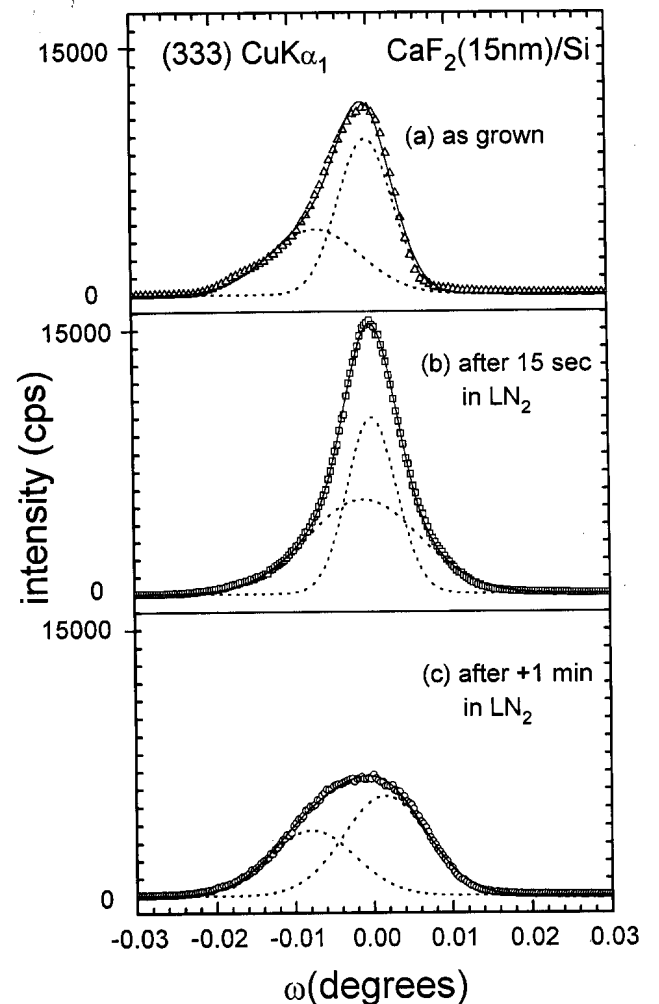


Figure 3. ω scan of the (333) Bragg diffraction peak of the CaF_2/Si structure after thermal cycles from 300 to 77K: (a) as grown sample, (b) after 15 sec immersed in LN_2 and (c) after +1 min immersed in LN_2 .

To simulate the real operating conditions of infrared detectors, a 15 nm thick CaF_2 layer on Si was submitted to various thermal cycles from 300 to 77K. Fig. 3 shows the HRXD spectrum of the sample measured after each thermal cycle. To distinguish between the two (333)

diffraction peaks in this structure, the spectra were fitted with a double Gaussian. As shown in Fig. 3b, after the first thermal cycle with 15 seconds immersion in LN₂ the CaF₂(333) Bragg peak shifts towards the Si(333) peak position causing an increase in intensity of the total peak $\omega(333)=\text{CaF}_2(333)+\text{Si}(333)$. However, after the second thermal cycle with +1.0 min immersed in LN₂ (Fig. 3c) the $\omega(333)$ structure broadens and decreases its intensity. For subsequent thermal cycles with larger periods of time, the form of this $\omega(333)$ structure remains almost the same as the one plotted in Fig. 3c. The broadening of the total x-ray rocking curve $\omega(333)$ is related to an increase in the defects density at the CaF₂/Si interface. This increase in defect density and the modification of the strain in the CaF₂/Si interface may cause some effects in the lead chalcogenides layers grown on top of the BaF₂/CaF₂/Si structure when cooled to the liquid nitrogen temperature.

V. Conclusion

As demonstrated by HRXD and Hall effect measurements, the control on the CaF₂ layer strain appears to be very important to optimize the Hall mobility of PbTe layers grown on Si with fluoride buffer layers.

The large difference in thermal expansion coeffi-

cients between CaF₂ and Si is responsible for the in-plane tensile strain observed in the CaF₂ layer grown on Si. The shift and broadening of the CaF₂(333) Bragg peak observed when submitting the CaF₂/Si structure to thermal cycles from 300 to 77K indicate that some degrading effect on infrared devices grown on top of the BaF₂/CaF₂/Si structure may appear.

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