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Prospects for 3C-SiC Bulk Crystal Growth

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Abstract

Despite outstanding properties, the development of 3C-SiC electronics continues to suffer from the lack of good quality, bulk 3C-SiC substrates. Up to now, there is no real seed and/or optimized growth processes. In this work, we address these two different issues. A two-step approach is shown, which couples the advantage of vapour-liquid-solid hetero-epitaxial growth of 3C-SiC on a 6H-SiC substrate for the seed formation and the ones of the continuous feed physical vapour transport method for the growth of the bulk material at reasonably high

rate. Using such an approach, we could combine the elimination of the twin boundaries which systematically form in the 3C/6H-SiC epitaxial system, with getting a growth rate of about 0.2 mm/h for the bulk material. An evaluation of results is done, with respect to the change in growth conditions.

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1. Introduction

Since the pioneering Silicon Carbide Conference in Boston, in 1959, the cubic form of the material which crystallizes with the zinc blende structure has been widely recognized as a promising wide band gap semiconductor. As a consequence, many literature works devoted to the crystal growth of the different SiC polytypes focussed primarily on the cubic form (also called 3C or β-SiC variant). Altogether, the following has been found.

First, using the standard Lely method, the formation of β-SiC is extremely rare but never completely impossible [1,2]. As a consequence, although the Acheson and Lely processes provided a lot of large 6H-SiC seeds for the development of the hexagonal variants, cubic SiC seeds were almost never obtained. In the case of self nucleated SiC crystals on graphite [3] some crystals of very high structural quality could be obtained [4], but the size was only several mm in diameter. This is not compatible with any potential (large scale) device application and, unlike the hexagonal 6H and 4H polytypes grown with the seeded sublimation method for electronic device applications [5,6] it never benefited from a large scientific and/or technological demand.

3C-SiC spontaneously appears in the range of 1500 to 2000°C, using either a solution [7] or a chemical vapour deposition (CVD) route [8-10] with or without added chlorine. In this way, in the recent years some highly significant results gave to 3C-SiC a renewed interest. This includes the hetero-epitaxial growth of β-SiC on large silicon or silicon on insulator substrates [11,12] , or the large area free-standing 3C-SiC wafers grown by hetero-epitaxy on a "undulant" <001>-Si wafer [13]. In this case, up to 6 inches diameter free-standing wafers were demonstrated but the 3C crystals still contain too many structural defects which, intrinsically, relate to the poor intrinsic thermal and lattice mismatch in the hetero-epitaxial SiC/Si system.

To summarize, up to now nobody succeeded in growing real 3C-SiC bulk single crystals.

Obtaining 3C-SiC wafers remains a challenging issue but, to be successful, there are two problems to solve. First, make available *large 3C-SiC seeds*. Second, develop a suitable *growth process*. Up to now the seeded sublimation growth, also called PVT (for physical vapour transport) method, remains the most common technique for the growth of 6H- and 4H-SiC ingots [5,6,14] but the high temperature involved (>2000°C) makes the stabilization of the β-SiC polytype extremely difficult [15].

In this work we will address successively these two issues. First, we will show that a high quality 3C-SiC layer can be grown from the liquid phase through a vapour-liquid-solid (VLS) mechanism on a commercial 6H-SiC substrate. Second, we will show that this layer can be used as a seed for the growth (at high rate) of a 3C-SiC single crystal. Then, some optical and structural evaluations of the resulting samples are made with respect to the growth conditions. Finally, the potentiality of such an approach is discussed and we show that it could pave the way of a future 3C-SiC electronics.

2. Experimental details

Cubic SiC seeds preparation. Starting from the <0001> on-axis Si face of a 6H-SiC seed, initial 3C-SiC layers were grown in a Si-Ge melt using the vapour-liquid-solid (VLS) growth technique [16]. The deposition was carried out at atmospheric pressure, in a homemade epitaxial apparatus equipped with a vertical cold wall reactor. The 6H-SiC seed was placed at the bottom of a graphite crucible and, in order to form a liquid phase containing 25 at% Si, both Si and Ge pieces were stacked on top of the seed. Then, they were heated under a purified Ar atmosphere, up to 1500°C. When reaching the temperature plateau, a 3 sccm flow of propane was added to start the real SiC growth. After 30 min deposition, propane was removed and the liquid was extracted (sucked up) before cooling. The remaining (small)

traces of Ge-Si alloy were eliminated by wet chemical etching in a HF–HNO_3 solution. For further details, see Refs. [16].

Bulk crystal growth. To enlarge the range of deposition conditions, two different PVT configurations have been used with, of course, the same geometry for the growth cavity. As shown in Figure 1b, we use a special cone-shaped guide in the deposition zone which is made in order to "concentrate" the species close to the seed surface. The net flux of sublimated species per unit surface being a direct function of the cone sections ratio we compute that, taking into account the top (small) and bottom (large) cone areas, the species concentration should be increased by (typically) a factor of 6.

The first configuration uses simply a close sublimation crucible, modified as previously explained, and a high purity 6H-SiC powder. For more details, see Figure 1a and Ref. [14]. The second one calls for the CF-PVT process (see Figure 1c and Ref. [17]) in which a polycrystalline SiC source is formed at the bottom of the crucible, and continuously fed from high temperature CVD. The standard gaseous precursor is TMS (Tetra-Methyl-Silane) diluted in argon. Below 2050°C, using TMS the CF-PVT process offers a specific advantage compared to PVT. Keeping the same thermal environment (thermal gradient) and pressure, it allows to tune the supersaturation close to the seed by simply changing the TMS partial pressure in the CVD zone. This is particularly true working under CVD limited process conditions [18]. Since TMS is not adapted for deposition (i.e. source feeding) at temperatures higher than 2050°C, we turned the difficulty by implementing the standard PVT configuration. In this way, we could work at higher temperature.

To optimize the growth conditions, several depositions were done directly on the graphite lid. In most cases, this led to the formation of 3C-SiC polycrystalline material.

Samples characterization. The polycrystalline material directly formed on the graphite lid through self-nucleation was first analysed by X-ray diffraction in the θ-2θ geometry. Then, a triple axis diffractometer was used for texture measurements. Concerning the single-crystals, high resolution X-ray reciprocal space mapping (RSM) was done. Then, we extracted the average stacking faults (SFs) density from the simulation of the diffuse intensity streaks. Details of the measurements and modelling technique have been given elsewhere [19]. Thin specimens were also prepared for birefringence microscopy, both in the planar view and cross-sectional mode. In both cases, in order to reduce the cumulative contribution of defects, the thickness of the specimens was reduced to ~ 70 µm by mechanical grinding and polishing. Finally, the specimens were thinned by ion milling for TEM (Transmission Electron Microscopy) examinations. Independently, low temperature photoluminescence (LTPL) spectra were collected at 5K using 20 mW from the 244 nm line of a FreD (Frequency Doubled) Argon-ion laser as excitation source. Detection was done using a Triax Jobin-Yvon spectrometer, fitted with a cooled CCD camera [20].

3. Results

3C-SiC seeding stage. Under the deposition conditions chosen in this work, the 3C-SiC layers obtained from the VLS technique were ~1 µm thick. They were free of double positioning boundaries (DPBs) which are a particular case of twins coming from the two possible orientations of the cubic 3C-SiC axis on the hexagonal 6H-SiC basis. The X-ray RSM analysis of the layers revealed also that they were free of SFs or, at least, below the detection limit of the method which is 100 cm^{-1}.

Cross-sectional TEM (X-TEM) observations collected at the substrate to overgrown interface are shown in Figure 2. They show the presence of microtwins (MTs), stacking faults (SFs)

and dislocations. The MTs appear along the entire interface between the 3C-SiC layer and the 6H-SiC substrate. The dislocations are formed at the 3C/6H interface but annihilate within the first few hundreds of nm from the interface. Finally, in all areas under observation, we notice that no SF is created at the 3C/6H interface.

Bulk crystal growth. To investigate the growth of the bulk (un-seeded) 3C-SiC material, native 3C-SiC polycrystalline ingots were grown on the graphite lid at temperatures above 2200°C (Figure 3). At high supersaturation, the growth rate was ~ 1.7 mm/h, and the average grain size ~ 10µm. The ingot were textured along the <110> direction. To reduce the nucleation density on the graphite lid, and promote the growth of a few single crystals, the supersaturation value was decreased. In this way, small 3C-SiC single crystals were obtained at 2050°C, with a few millimetres diameter (Figure 4a). The price to pay was a reduction of the growth rate to ~ 0.2 mm/h. In most cases, such crystals exhibit well-developed facets, typical of the 3C-SiC space group. This is shown in Figure 4b. Notice also that, in some cases, a few twins can be suspected as indicated by the presence of re-entrant dihedral angles.

Seeded growth. Once the growth conditions have been adapted to the stabilization of the 3C polytype, they can be transposed to the seeded SiC growth. Of course, to check the interest of VLS, one hetero-epitaxial growth has to be done directly on a <0001> 6H-SiC substrate and compared with a homo-epitaxy done on a 3C-SiC layer grown by VLS. In both cases we used identical growth conditions, similar to the one used for the samples shown in Figure 4. The only difference between the two processes was the seed surface condition. It was "Epi-ready^{TM}" according to the well-established Novasic process for the 6H-SiC substrate [21] and as-grown for the 3C-SiC VLS layer. This means that, in the latter case, the surface was strongly step-bunched, which is typical of liquid phase layers. In both cases, the growth rate

was ~ 150 μm/h.

In Figure 5 we compare two birefringence microscopy pictures obtained from cross-sections prepared in a) the 3C-SiC crystal grown directly on a 6H-SiC substrate and b) the 3C-SiC crystal grown on the 3C-SiC layer formed by VLS on a 6H-SiC substrate. We notice the following. Without VLS seeding the 3C-SiC crystal presents a high density of DPBs which form at the 3C-6H interface. They propagate all along the crystal length and, in the vicinity of these DPBs, a lot of microtwin lamellae (MTLs) can be observed which build at specific angles with respect to the surface of the seed. These MTLs lie along the dense {111} planes and, depending on the direction of observation, appear with linear or trapezoidal shapes. Since a perfect 3C-SiC crystals and/or a pure 3C lamella should not give any contrast using birefringence microscopy, this suggests some local optical anisotropic perturbation. Indeed, after KOH etching, it was found that all MTLs consist in a set of closely located stacking faults which might bring some local lattice anisotropy. This is why they appear clearly in birefringence imaging. With VLS seeding, the 3C crystal appears free of DPB and the MTLs density is drastically reduced. X-ray RSM reveals a SFs density of about 2.2×10^4 cm^{-1} to 4×10^4 cm^{-1} for the samples grown on 3C-VLS seed and on 6H-SiC seed respectively, while more local measurements by planar-view TEM (PV-TEM) give $5.8x10^3$ cm^{-1}.

In Figure 6 we show an example of low temperature luminescence spectrum collected at 5K. On this sample, we resolve all usual near band edge (NBE) features of low temperature, high quality, 3C-SiC recombination spectra. For a recent review, see Ref. [20]. They have been labelled ZPL (for Zero Phonon Line) with TA, LA, TO and LO-phonon replicas. The index 1 means that there is only one exciton bound to the recombination centre. On this picture appear also much weaker extra features. First is the weak (intrinsic) I_{TA} line. It comes from the radiative recombination of a free exciton with emission of a TA (46 meV) phonon and gives

for the 3C-SiC excitonic bandgap at 5K a value of Eg(X)= 2.389 eV. This is in excellent agreement with previous literature data and evidences a high quality, strain-free, material. Second there are the companions lines of the main (m=1) NBE exciton features. These are multiple bound exciton complexes (MBEC) which have been labelled m=2 to 5 to indicate the number of electrons and holes which participate in the final (excitonic) molecule.

Such multiple bound exciton features are a specific signature of the low temperature luminescence spectra of high quality 3C-SiC single crystals. They have only been reported in a few works (see, for instance, Ref.[20] and references therein) performed on a few specific samples. This is because, basically, three conditions must be fulfilled before they can be observed : 1) one needs high enough excitation intensity in order to create more than one single exciton per recombination centre. This makes the LTPL spectrum excitation-density dependent ; 2) one needs a low density of recombination centre (i.e. a high quality material) to fulfil more easily condition #1 ; 3) one needs a rather long carrier lifetime (i.e. again a high quality material) to give a chance to the extra-excitons (m=2, 3…5) to bind and not to recombine directly as intrinsic luminescence lines, like the I_{TA} feature of Figure 6.

4. Discussion

3C-SiC seed. To the best of our knowledge, the VLS mechanism is the only process which has demonstrated ability to produce in a reliable and reproducible way DPB-free 3C-SiC layers on a commercial hexagonal substrate. The precise mechanism involved in the complete 6H to 3C transition and the complete selection of only one crystallographic variant among the two possible (DPB elimination) is currently under investigation and will be the focus of future papers. The dislocations formed within the layer are rapidly annihilated within the first µm. The SF density is very low in such liquid phase grown layer. This could probably be related to

the absence of DPB. It is indeed well known that the high elastic energy created by those incoherent twin boundaries is relaxed by the formation of SFs [22]. Single domain 3C-SiC layers grown by VLS can thus be considered as high quality seed for the subsequent growth of 3C single crystals.

Growth process. It has been claimed for a very long time that 3C-SiC is a metastable form. Some proofs in this direction have been given by Hamilton et al. [1] when they observed the formation of a 3C layer during the cooling of hexagonal platelets in the Lely process. Also, the growth of 3C-SiC requires a strong deviation from equilibrium and/or a low temperature [2, 23]. The higher the process temperature, the larger the deviation from equilibrium should be in order to stabilize the 3C polytype. As a consequence of its metastability, a solid-state 3C to 6H transition is usually encountered at temperatures higher than 2000°C, and starting from 1800°C [15]. Following such observations, we have adapted our standard PVT process to reach high supersaturation levels. In this way, in those experiments, we succeeded in stabilizing the cubic polytype at a temperature higher than 2200°C. The small grain size, about 10 µm in diameter, is related to the high supersaturation. Decreasing the supersaturation reduces the nucleation rate and promotes crystal enlargements. With the CF-PVT methode, we were thus able to select a few crystals and make them grow (Figure 4a and b). The crystals, up to a few mm in diameter, were perfectly facetted. Altogether, our results suggest growth conditions close to the thermodynamic equilibrium. We conclude then that a strong deviation from equilibrium is not necessary to stabilize the cubic polytype even at high temperature. This shows that the temperature is ***not*** the only parameter to consider for the 3C to 6H solid state transition.

Starting from now, it is important to remember that all 3C-SiC crystals grown at high temperature (>2000°C) have been obtained through self nucleation, usually on graphite. This

is true in this work, at 2050°C, but also at 2350°C in the work of Omori et al. [24] and, at even higher temperature, for the 3C-SiC platelets sometime found in the Lely process [1,2]. This means that under particular conditions, most probably under strain-free conditions, 3C-SiC can be grown close to the thermodynamic equilibrium without any 3C to 6H phase transition. Said in a different way, depending on the stress state, the critical temperature for the 6H-3C phase transition can be shifted from 2000°C up to 2300°C or more. This solid-state transition is still far from being understood and even the mechanism and the driving force have not been clearly identified. Simply, and contrary to most literature results, it seems that the sublimation process can be adapted to the growth of the 3C-SiC polytype, at high temperature, reasonably high rate and under near equilibrium conditions.

A direct transposition of the growth conditions used for self-nucleation to the seeded conditions allowed us to form a 1 mm thick 3C-SiC single crystals after 5 hr growth (see Fig.7). The use of a DPB-free 3C-SiC layer formed by VLS as seed has resulted in significant improvement of the crystal quality as, for instance, on the MTLs density. However, still, the SFs density is higher in the CF-PVT part of sample than it was in the VLS seed. This could originate from the starting surface of the VLS layer which, being as-grown, is very rough. This point will be investigated in a future work. Already, the LTPL spectra collected at 5K in a DPB-free crystal present an excellent resolution of near band edge excitonic features, with MBEC resolution up to m=5. This evidences the high optical and electronic quality of our 3C-SiC material and constitutes a most promising result for the development of high quality 3C-SiC wafers.

5. Conclusions

We have demonstrated that the VLS process is well suited to produce high quality, DPB free, 3C-SiC layers on a 6H-SiC substrate. Such layers contain a low density of SFs. They are then well adapted to be used as seed for bulk 3C-SiC single crystal growth. Cross-linking our results with the results coming from the literature brings out to the conclusion that the 3C to 6H phase transition is not correctly identified and could be avoided even at high temperature if conditions close to thermodynamic equilibrium are completed. With this two steps process, (111) oriented 3C-SiC crystals have been grown at high rate (0.15 mm/h) with high intrinsic purity. Improvement of the crystal quality is now under investigation but our results should open the way of bulk 3C-SiC “ingot”.

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Figure Captions

Figure 1: Schematic representation of a) a standard PVT crucible and c) the CF-PVT one. In b) is shown a digital X-ray radiography of the PVT cavity. It is the same in both configurations. The cone-shaped guide allows an increase of the supersaturation value, close to the seed, by a factor of ~ 6.

Figure 2: Sequence of XTEM micrographs showing i°) the formation of microtwins (MTs) along the entire 3C/6H interface while ii°) the stacking faults (noticed SFs) appear only after some hundred nanometres growth.

Figure 3: 3C-SiC polycrystalline ingot grown on a graphite lid, under high supersaturation conditions at T>2200°C.

Figure 4: Self nucleated 3C-SiC single crystals obtained under "low supersaturation" conditions at 2050°C using the CF-PVT process : a) full-size view on the graphite lid ; b) binocular picture of an isolated 3C-SiC crystal, with perfect optical facets.

Figure 5: Birefringence microscopy observations performed on two cross-sections prepared in 3C-SiC crystals grown a) directly on a 6H-SiC substrate and b) on a thin 3C-SiC layer formed by VLS on a 6H-SiC substrate. The grey level indicated as "no birefringence" means that the magnitude of birefringence is zero. If the grey level is lighter or darker, this means that the magnitude of birefringence differs from zero, as is the case for instance for Microtwin Lamellae (MTL).

Figure 6 : Example of the LTPL spectra collected at 5K. Notice the presence of MBEC, up to m=5. This appears only on high quality 3C-SiC material.

Figure 7: Pictures of an as grown 1 mm thick layer grown on a VLS seed. The size of the sample is 9*9 mm².

Figure 1

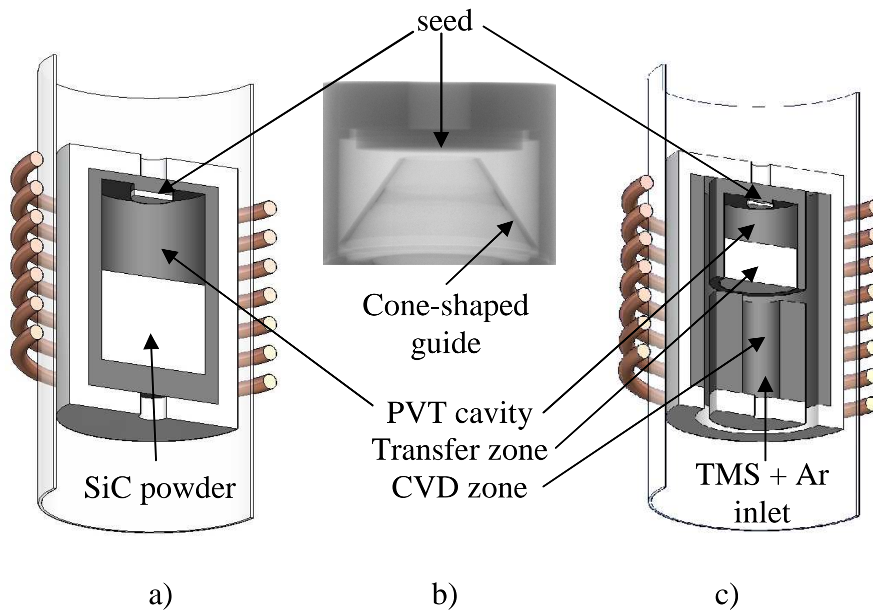


Figure 2

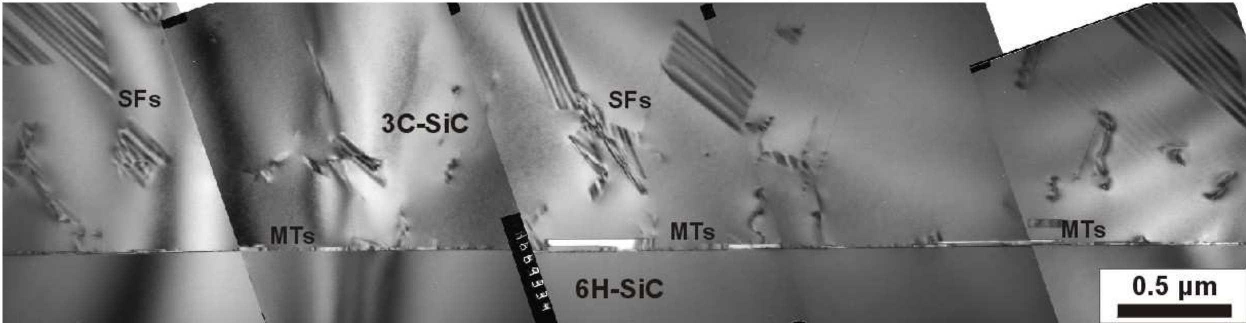


Figure 3

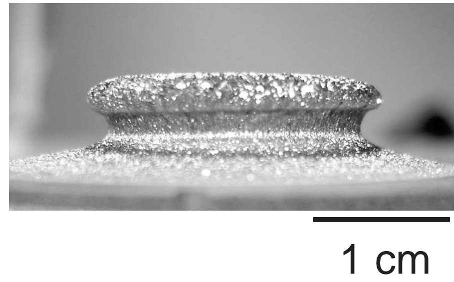
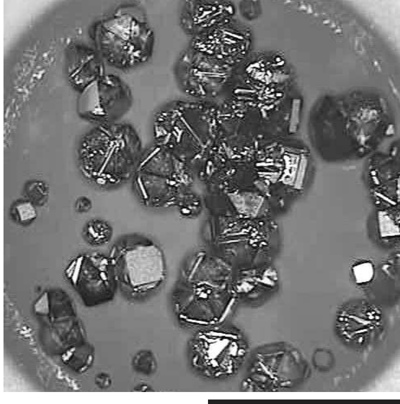


Figure 4



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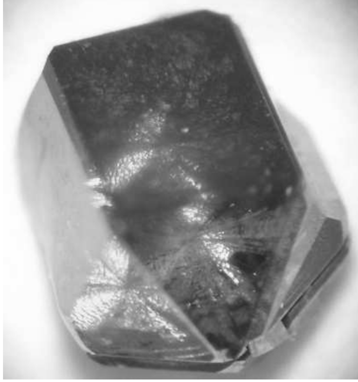
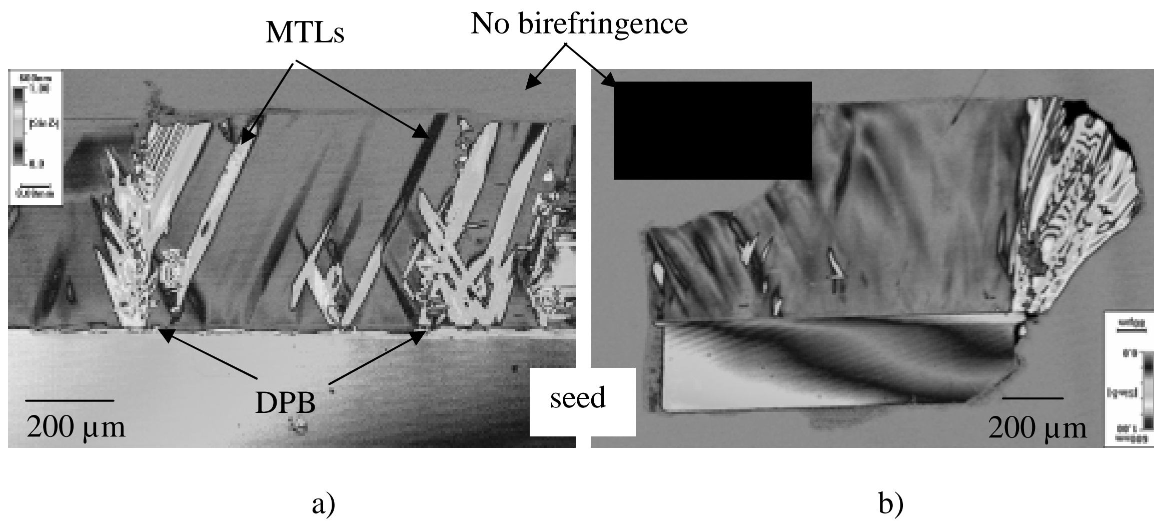


b)

Figure 5



a) b)

Figure 6

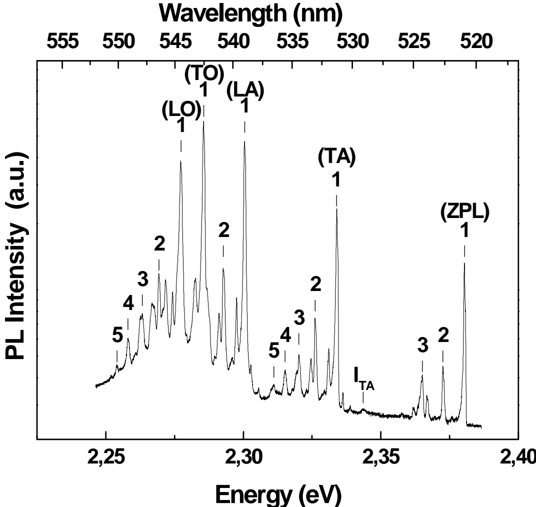
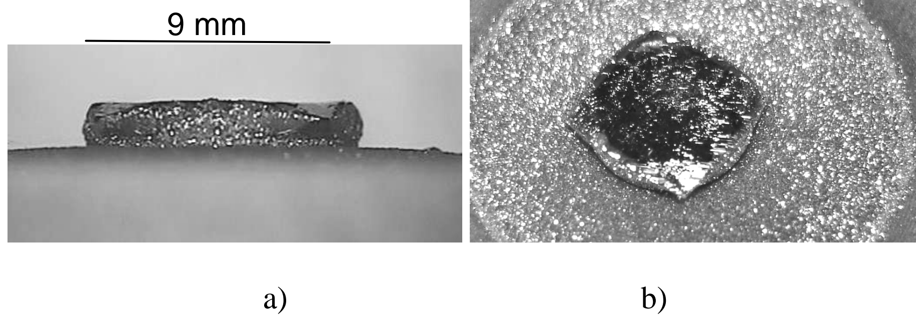


Figure 7



a) b)