Selective Growth of CdTe on Patterned CdTe/Si(211)

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Abstract

We have studied selective growth of cadmium telluride on Si(211) by molecular beam epitaxy (MBE). Patterned substrates were produced by optical lithography of MBE-grown CdTe/As/Si(211). Photoemission microscopy was used as the main tool to study selective growth. This is very powerful because Si or SiO_2 can be distinguished very easily from areas covered with even small amounts of CdTe due to contrast from workfunction differences. It was found that CdTe grows on CdTe without sticking on bare Si areas if the temperature is sufficiently high. Based on analysis of the temperature dependence of the growth rate of CdTe, we suggest that different physisorption energies on Si and CdTe are the main cause of this selective growth.

1. Introduction

CdTe or CdZnTe are widely used as buffer layers for the epitaxy of HgCdTe. Among the polar faces of CdTe, only the tellurium-terminated orientations are suitable for the growth of HgCdTe by MBE [1]. IR detectors and focal plane arrays require CdTe substrates with high purity and low defect density. Although monocrystalline layers of CdTe have been grown directly on silicon since 1989 [2] and successful fabrication of detectors from HgCdTe grown on such layers has been demonstrated [3,4], the large lattice mismatch between CdTe and Si (19%) and the different thermal expansion coefficients continue to be a challenge. Dislocations that appear at the interface between CdTe and Si can propagate into the active layer and lead to a decrease in performance or premature failure of the devices.

Theoretical and experimental studies by Zubia *et al.* [5] demonstrated that the use of nanostructures as seeds for selective epitaxy of a semiconductor can result in new relaxation mechanisms that would lead to lower defect density of the grown layer. Guha et al. [6] have demonstrated defect reduction through MBE growth of III-As compounds on nanosize mesas while Hiramatsu et al. [7] and others have demonstrated defect reduction through growth of III-nitrides by MOCVD by epitaxial lateral overgrowth starting from nanostructures. Selective growth of CdTe was demonstrated by MOCVD by Bhat and Zhang.[8]

In the present study, we demonstrate that selective growth can be achieved by molecular beam epitaxy on CdTe islands patterned on Si(211) and we propose a mechanism based on a change of the physisorption energy to explain the selectivity. The CdTe islands patterned on the silicon substrate are micron-size diameter. To characterize these structures, we use mainly in-situ photoelectron emission microscopy (PEEM), X-ray photoemission spectroscopy (XPS),

scanning electron microscopy (SEM), surface profilometry and Nomarski microscopy.

2. Experimental details

We started with the growth of thin layers of CdTe on Si(211). These layers were then patterend by optical lithography to produce cylindrical islands of CdTe with areas of bare Si between the islands. These patterned layers were then used as templates for selective growth.

For the initial growth of CdTe on Si(211), the UHV system is composed of an introduction chamber, a preparation chamber (base pressure of $5x10^{-10}$ torr) and a MBE growth chamber (RIBER OPUS 45) equipped with RHEED (base pressure of $8x10^{-10}$ torr). The substrates are 3 inch Si(211) wafers and are placed on 5 inch molybdenum holders. The flux from the MBE cells is measured with a Bayard-Alpert gauge placed between the cryopanel and the substrate holder. In the preparation and the growth chambers, the temperature is measured with a type-K thermocouple placed behind the substrate. The real substrate temperature is always lower than the thermocouple reading, but for simplicity, we will quote the thermocouple reading throughout this paper.

After patterning, the height of the CdTe islands is measured ex-situ with a Veeco 8 DekTak step profiler. X-ray diffraction (XRD) is used to determine the crystal structure and scanning electron microscopy (SEM) and scanning Auger microscopy (SAM) to check the homogeneity of the patterned substrates.

Selective growth was studied in an in-situ UHV system that consists of an introduction chamber, an analysis chamber with Auger electron spectroscopy (AES) and photoelectron emission microscopy (PEEM) (base pressure of $6x10^{-11}$ torr) and a RIBER MBE chamber (base pressure of $5x10^{-10}$ torr). The PEEM experiment uses a Hg lamp (energy of 4.9 eV) and the pictures are

recorded with a Peltier-cooled CCD camera. The temperature in the in-situ MBE chamber is measured indirectly via a reference table giving the temperature of the sample holder vs the heating power. This temperature is not the real surface temperature of our samples and is not directly comparable to the temperature measured in the OPUS MBE chamber. However, temperature differences observed in the two MBE systems are expected to be similar, at least over a limited range. The flux is measured by a Bayard-Alpert gauge placed behind the substrate.

3. Results

a) *Growth of CdTe/As/Si(211) and patterning of the substrate*

A 3 inch Si(211) wafer was cleaned using a method adapted from the RCA process.[1] This method includes etching in NH_4OH:H_2O_2:H_2O, HF:H_2O and HCl:H_2O_2:H_2O solutions. It leaves a thin protective oxide (about 1 nm) on the Si surface. At the end of the process, the sample was dried with nitrogen and directly transferred into the introduction chamber. The substrate was outgased in the preparation chamber for 5 hours at 500°C and the Si oxide was desorbed in the growth chamber by heating to about 1050°C for a few seconds. The sample was then cooled to 400°C under As_4 flux (pressure = $5x10^{-7}$ torr). At 310°C, a CdTe nucleation layer was grown for 2 min (pressure = $1x10^{-7}$ torr). The substrate was annealed under Te flux (pressure of $5x10^{-8}$ torr) for 10 minutes at 460°C, followed by growth of CdTe at 380°C for 2 hours.

The thickness, measured with the profilometer, is 2µm. XRD shows a major (211) orientation and a small peak related to the (331) orientation. This is expected when CdTe is grown directly on Si(211).[2] In a separate experiment, we grew true single-crystalline CdTe(211) on Si(211) with a thin intermediate layer of ZnTe. These layers were not used for the present work; they will be used for a detailed study of the crystalline quality of CdTe grown selectively on nanoscale CdTe

seed areas on Si(211).

The CdTe/As/Si(211) samples were then patterned by optical lithography. This produced islands of CdTe on the Si(211) substrate, as observed by SEM, SAM, XPS and Nomarski microscopy. The CdTe islands have a diameter of 80, 100, 160 and 320 µm (figure 1).

b) ***Preliminary experiment***

In order to achieve selective growth of CdTe, one must know the highest temperature where CdTe can nucleate on Si(211) passivated with arsenic and the lowest temperature where CdTe desorbs from Si. These temperatures were determined in the in-situ MBE chamber.

To determine the highest nucleation temperature of CdTe on Si, the flux of CdTe is set to a constant value ($5x10^{-7}$ torr) and a clean Si(211) substrate passivated with As is set to a starting temperature of 450°C for 30 minutes. The sample is then exposed to the CdTe flux for 2 minutes. If we do not notice any change in the RHEED pattern, the substrate temperature is decreased by 10°C and the experiment is repeated. By this method, we find the highest nucleation temperature of CdTe on Si(211) to be below 400°C.

For the lowest desorption temperature of CdTe, an as-grown piece of the 3 in. CdTe/Si wafer is etched in a 0.1% bromine methanol solution for 5 seconds before its introduction in the in-situ UHV system. The Te-excess produced by the etching is removed by heating the substrate to 310°C. The sample is then heated to 400°C for 30 minutes. If the RHEED pattern remains the same, the temperature of the sample is increased by 10°C. The lowest desorption temperature is found when a RHEED transition is observed where the pattern changes from CdTe to Si(211). We determined this temperature to be 480°C.

In conclusion, we expect it to be possible to achieve selective epitaxy of CdTe if the substrate

temperature is between 400°C and 480°C. In this case, the CdTe should stick only on the CdTe islands and not on the silicon substrate.

c) ***Selective growth experiments***

To check this selective epitaxy process, 3 samples of patterned CdTe islands on Si(211) were etched in a 0.1 % bromine methanol solution for 5 seconds. One was kept as reference to measure the height of the islands before the selective growth process (figure 2a). At this point, the height of the island is 0.8 μm. The two other samples were loaded into the in-situ UHV system. They were heated to 310°C to remove the Te-excess. The surface of the in-situ samples was then checked by PEEM (figure 2b). The work function of SiO_2 and CdTe is 4.52 eV and 5.90 eV, respectively. Hence, with an excitation source of 4.9 eV, the CdTe islands appear black on the picture and the SiO_2 is bright (we consider the work function of SiO_2 because this compound was detected by AES). In order to study the selective growth, one sample was set to 400°C and the second one to 420°C while they were exposed to the same CdTe flux (pressure = $5x10^{-7}$ torr) for 2 hours.

At 400°C, the islands grow siginficantly both in diameter and in height (figure 3a and 3b). However, it is obvious from the PEEM images that small features appear between the islands (figure 3d). Because these features appear dark in PEEM, we suggest that they are CdTe islands that nucleate at random positions on the Si surface if it is exposed to the CdTe flux for an extended period. These structures are very rough and their height varies from 1 to 3 μm. For the islands, a vertical growth rate of 1.4 nm/s was calculated from the step profile measurements. For the additional structures, the average height is 2.5 μm with a standard deviation of 1.2 μm.

In summary, although RHEED suggested that CdTe would not nucleate on As/Si(211) at

temperatures of 400°C or higher, this temperature is still too low to avoid deposition of CdTe on silicon. It means that the nucleation rate is very slow, but once a small structure of CdTe is formed on the surface, the growth rate increases because this seed acts as a preferential growth site for CdTe.

When the substrate temperature was raised to 420°C, we only observed an increase in the height of the island (figure 4a) without any additional dark features visible by PEEM between the islands (figure 4b). The height of the island after 2 hours of growth is 1.53 µm ± 0.02 µm, confirming that CdTe indeed grew on the islands. The growth rate is much lower than at 400°C, about 0.2 nm/s. The absence of any features in the PEEM images between the CdTe islands confirms that selective growth was achieved at 420°C.

4. Discussion

We will now propose an explanation of the mechanism of selective growth based on the temperature dependence of CdTe growth rate. In MBE, the growth rate is conveniently measured by RHEED oscillations. Such oscillations are not observed in the case of CdTe(211)/As/Si(211), but they were used in an earlier study[1] to measure the growth rate of CdTe on As/Si(111).

In this study, the lowest temperature where nucleation of CdTe on As/Si(111) is not observed was found to be 270°C based on RHEED experiments and the lowest temperature where CdTe desorbs completely from Si(111) was 350°C. As we have mentioned before, these temperatures cannot be compared directly to the thermocouple readings in the present work, and we have shown in our present work that the nucleation temperature determined from RHEED experiments is not completely accurate. Yet it is significant that the difference between these temperatures is 80°C in both the earlier study on Si(111) and in our present work on Si(211).

In the earlier tudy, the growth rate of CdTe was measured as a function of substrate temperature. Here, we use the model developed by Behr *et al.* [1] for the growth of CdTe(100) to fit these experimental data. Their model involves two thermally activated processes, which they interpret as physisorption and chemisorption respectively. The equation, with the parameters determined from a least-squares fit to the data for $CdTe(\bar{1}\bar{1}\bar{1})B$ /As/Si(111), is as follows:

$$R\ (ML/s) = 3.46 - 28\exp(-E_{phys}/kT) - 2.23\times10^{15}\exp(-E_{chim}/kT) \qquad (1)$$

$$\text{with } E_{phys} = 0.14\text{eV and } E_{chim} = 1.88\text{ eV}$$

The result is shown in figure 5.

In the case of growth of CdTe on $CdTe(\bar{1}\bar{1}\bar{1})B$, each Cd atom has one bond with a Te atom below and three bonds with Te atoms above. For Te, the situation is the opposite. Hence, the rate limiting processes are physisorption of Cd on a plane of Te and chemisorption of Te on a plane of Cd since Cd atoms will quickly re-evaporate if they are not stabilized by Te atoms on top.

In order to understand the selectivity of growth of CdTe on $CdTe(\bar{1}\bar{1}\bar{1})B$ vs. nucleation on As/Si(111), we have tried changing the activation energies in eq. (1) until we obtained a curve that would give zero growth rate at 270°C (lowest temperature where nucleation is not observed by RHEED on Si(111).) This can be achieved by reducing the chemisorption energy to about 1.55 eV, or by reducing the physisorption energy from 140 meV to 98 meV (dashed line in figure 5). However, it is not likely that the chemisorption enrgy changes from 1.88 eV to 1.55 eV when the substrate is changed from CdTe to Si, since in both cases, Te chemisorbs on Cd. The only difference is that Cd has one bond to As-Si in one case, and one bond to Te in the other. Hence we suggest that the selectivity is due to lower physisorption energy on As/Si vs. CdTe.

An ideal CdTe(211) surface is composed of steps and (111) terasses. The bonding between Cd

and Te atoms is similar to the case of $CdTe(\bar{1}\bar{1}\bar{1})B$. Hence we suggest that the explanation of selectivity between growth on As/Si(211) and CdTe(211) is similar to the case of the (111) orientation. This is consistent with the measured difference between the highest nucleation temperature of CdTe on Si and the CdTe desorption temperature from Si for the two orientations.

5. Conclusion

Selective growth of CdTe on patterned Si(211) was achieved by MBE. First, a layer of CdTe was grwon on As/Si(211) and a pattern was etched by optical lithography. Selective growth was obtained because CdTe does not nucleate on Si while still growing on CdTe if the substrate temperature is sufficeintly high. Based on analysis of the temperature dependence of the growth rate of $CdTe(\bar{1}\bar{1}\bar{1})B$, we suggest that selective growth is possible because the physisorption energy is slightly smaller on Si than on CdTe.

It was shown by photoemission microscopy that the temperature for selective growth must be somewhat higher than the highest nucleation temperature for CdTe on As/Si(211) determined by RHEED; otherwise, CdTe will eventually nucleate on Si between the CdTe seed areas if the substrate is exposed long enough to the CdTe flux. This suggests that, besides the simple selectivity mechanism based on physisorption energies, nucleation around defects or impurities may play a siginificant role.

Figure captions:

Figure 1: SEM picture of CdTe islands patterned on Si(211)

Figure 2: a) Height of CdTe island after etching CdTe/As/Si(211), measured by step profilometer b) PEEM image of patterned CdTe.

Figure 3: After growth at 400°C: a) height of CdTe island by step profilometer; b) PEEM image of CdTe island; c) height of additional CdTe features by step profilometer; d) PEEM image of CdTe additional features.

Figure 4: After growth at 420°C: a) height of CdTe island by step profilometer; b) PEEM image of CdTe island.

Figure 5: Experimental points (squares) for the growth of CdTe on Si(111) are fitted (straight line) by a sum of two exponential decays. The dashed line represents CdTe growing on Si(111) and is obtained with the same equation than the fitted straight line except that the physisorption energy is reduced from 140 meV to 98 meV.

Figure 1

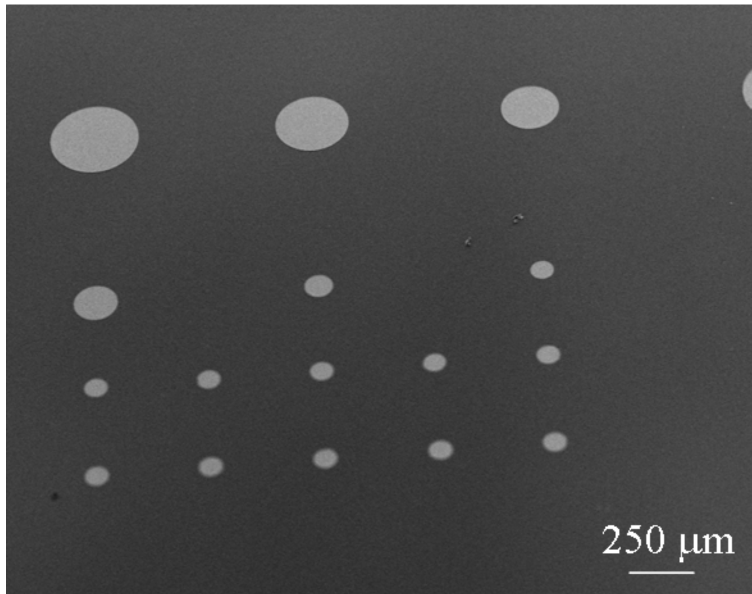
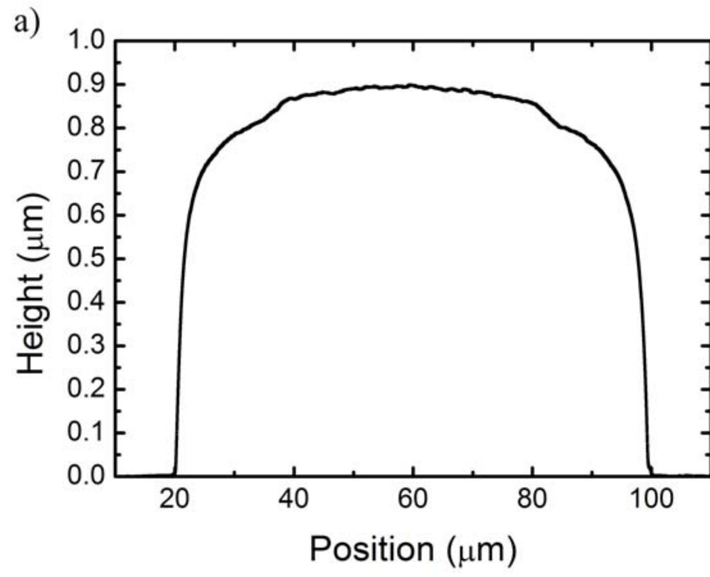


Figure 2



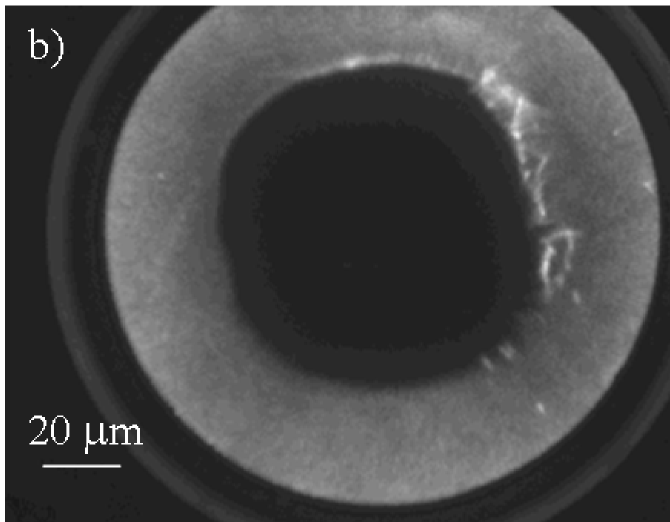
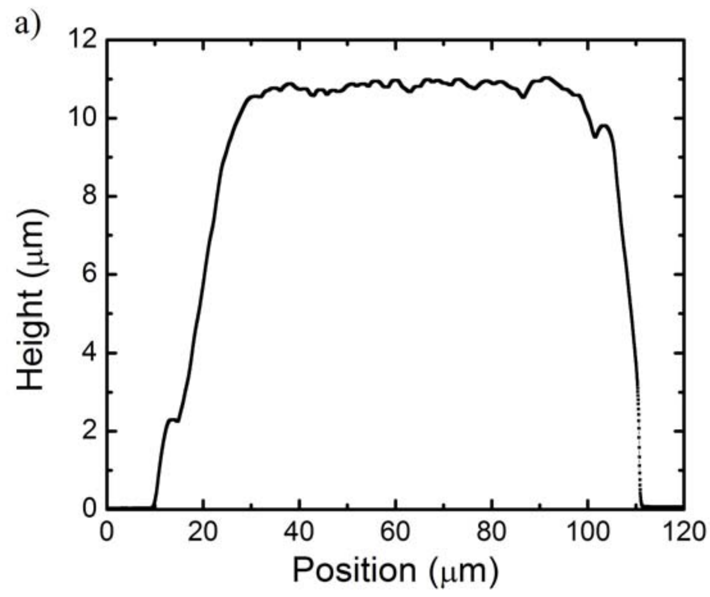
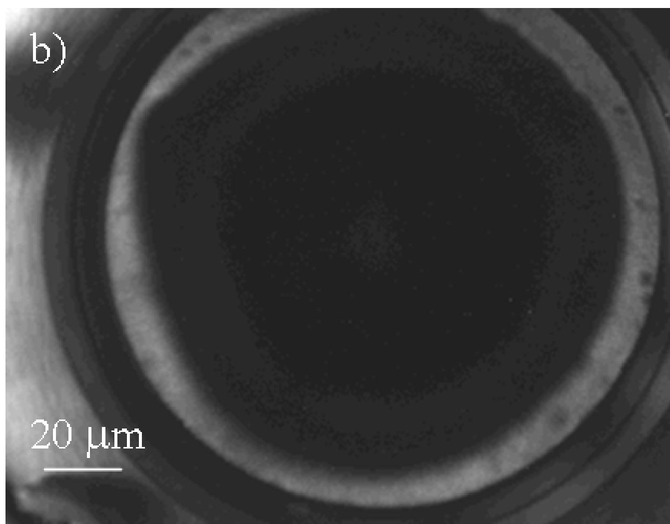
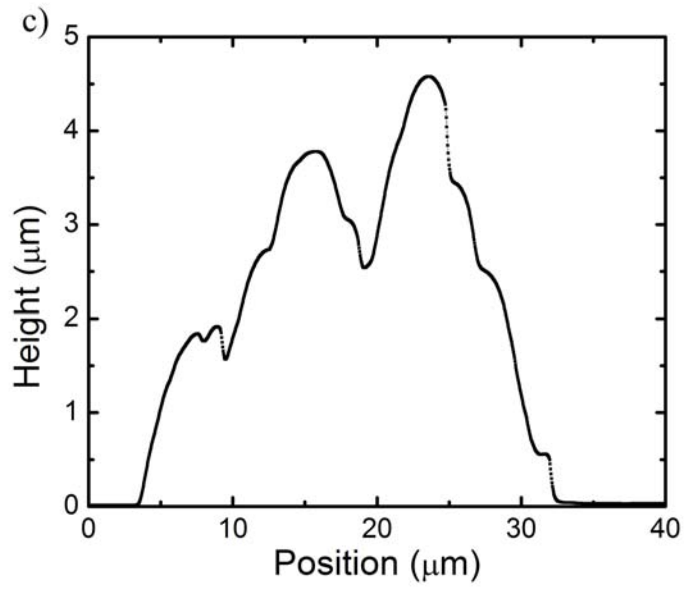


Figure 3



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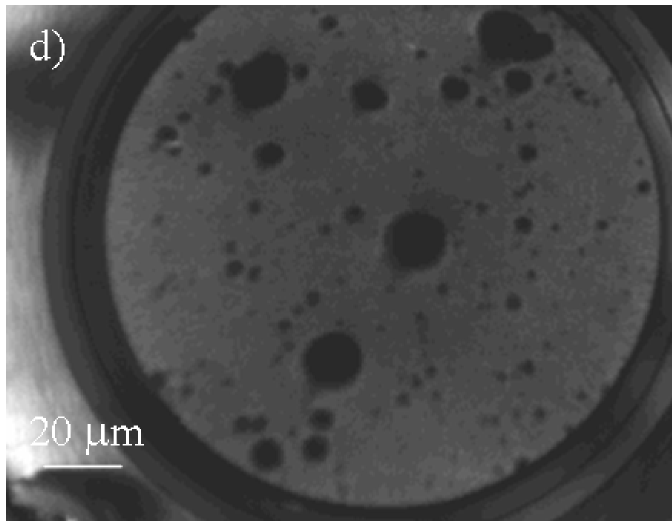
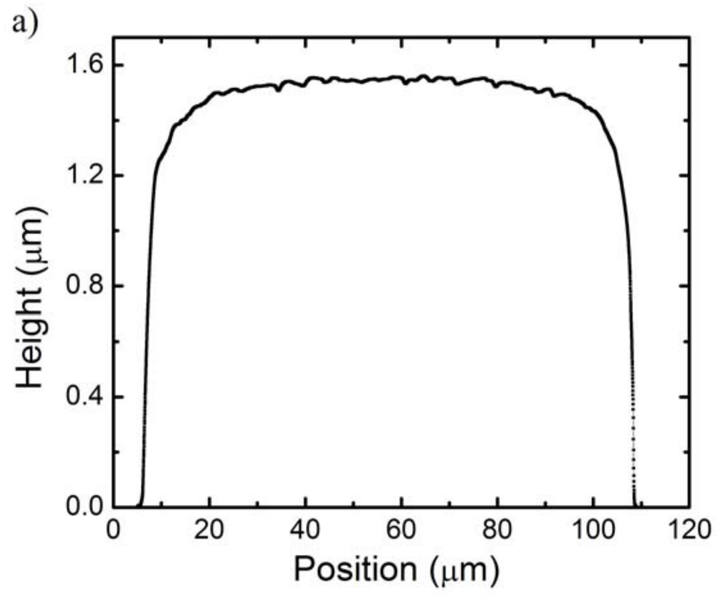

d)
20 μm

Figure 4



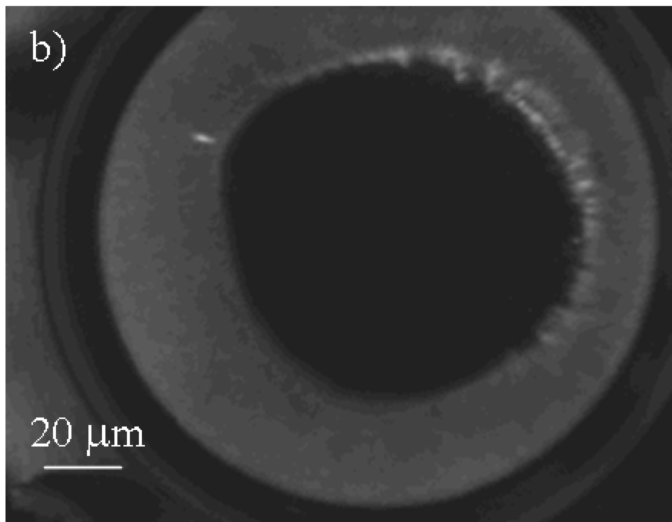
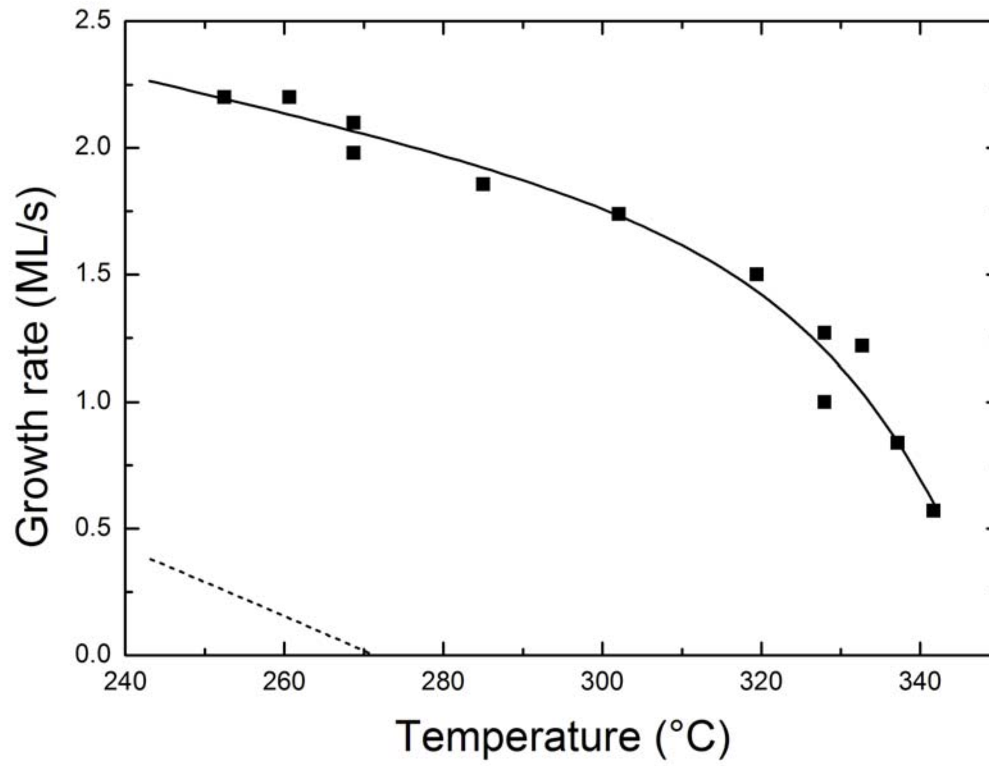


Figure 5



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