Evolution of wurtzite CdTe through the formation of cluster assembled films

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An approach has been developed to produce CdTe films with a high proportion of the metastable wurtzite phase. It involves the use of pulsed laser deposition to produce CdTe nanoparticles which are then collected on a substrate. Electron microscopy indicates that the nanoparticles produced have a relatively minor fraction of the wurtzite phase coexisting with the stable zinc blende phase. If these same nanoparticles arrive at a heated substrate they form a relatively dense cluster assembled film with an obvious wurtzite signature. Quite remarkable is that higher temperatures promote the metastable structure at the expense of the stable zinc blende phase. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357033]

CdTe is a well established photonic material that is widely used in infrared imaging applications. It has also attracted attention for its potential use in nonlinear optical devices and as a solar cell material.1 For all of these applications, the production of high quality films is crucial. Great strides have been made in this regard using thin film fabrication techniques such as molecular beam epitaxy (MBE),2,3 metal organic chemical vapour deposition4 and close-spaced sublimation (CSS).5 There exists, however, growing evidence that these nominally pure zinc blende (ZB) films are contaminated by thin wurtzite (WZ) layers. The formation of these layers has been associated with the existence of a high density of planar defects. Careful analysis of the CSS deposited films show that these planar defects tend to form near the interface regions and become more pronounced at high film growth rates or where substrate surface contaminants are present.6 Similar planar defects have also been observed in (111) CdTe films deposited using MBE. Many of the problems associated with the interface have been substantially reduced by depositing the films on miscut (001) Si substrates.7 In this case, planar defects form during the nucleation stage, but as the growth proceeds, a single-crystal film forms with a dominating domain that overgrows all other minority domains. Nevertheless, buried WZ layers may still exist, compromising the electrical properties of ZB CdTe films and leading to degradation in device performance. Thus, the formation of the WZ phase is of importance both from determining its influence as a parasitic phase and from obtaining an understanding of its growth kinetics, which in turn could result in thin film growth processes that will inhibit its formation.

The inclusion of small amounts of the WZ phase in nominally phase pure ZB films is not especially surprising. Cadmium telluride, like other II-VI compounds, can exist in both the ZB (cubic) and WZ (hexagonal) crystal structures and for the most part the energy difference between these two phases is small.7 For the case of CdTe, the equilibrium ZB phase is relatively well known and characterized compared to its WZ phase which is poorly understood because it is metastable8 and difficult to produce in a pure form.

Both WZ and ZB phase nanoparticles have been observed with varying populations depending on the II-VI material and the growth pathway.9,10 Applications have been developed which take advantage of tuning the photoluminescence through size effects.11 More recent has been the discovery of polytypism on the nanoscale12 in the form of a CdTe tetrapod structure with three of the arms exhibiting the WZ phase and the fourth showing a ZB structure. These examples demonstrate the promise of tailoring the material properties of II-VI semiconductors through size effects. In this letter, we will show a result where nanoparticles are used as intermediate growth step rather than a final product. By first producing nanoparticles using pulsed laser deposition (PLD) and then assembling a continuous CdTe film, remarkably we have found that it is possible to thermally promote the formation of the nonequilibrium WZ phase over the stable ZB phase.

PLD has proven itself to be a versatile research tool in the production of a diverse range of material systems. In this technique, pulses of ultraviolet light from an excimer laser are used to vaporize a bulk target resulting in a plume of atomic species that expands rapidly into vacuum in a direction normal to the target’s surface. The material ejected from the target then lands on a heated substrate where, under suitable conditions, it will form a single phase epitaxial thin film. High quality CdTe films, with a ZB structure, have been deposited on a variety of substrates using this technique.13 More recently, PLD has shown its usefulness in the formation of nanoparticles.14 In this scenario, the usual rapid expansion of material from a target is inhibited by a high pressure background gas giving rise to the densities, time scales,
and energies needed to reconstitute CdTe nanoparticles within the gas phase. Provided that the substrate is at a distance much greater than the extent of the plume, these nanoparticles will eventually settle out of the background gas and land on surfaces where they can be harvested.

The excimer laser used to create the nanoparticles operates at 248 nm with a pulse duration of approximately 20 ns. The pulses were focused onto a polycrystalline CdTe target with an energy density of 2 J/cm². The deposition chamber was evacuated to a base pressure of 10⁻⁷ Torr and then back-filled with ultrahigh purity helium gas to a pressure of 100 Torr. Nanostructures that were deposited on a transmission electron microscopy (TEM) carbon-supported Cu grid, placed approximately 3 cm from the target, were analyzed using a JEOL 2010F transmission electron microscope operating at 200 kV. The microscope is equipped with a Si(Li) ultrathin polymer window energy dispersive detector (Oxford Instruments) and a Gatan imaging filler Tridiem imaging system and spectrometer (Gatan). In Fig. 1, a variety of nanostructures can be observed: firstly, large, spherical particles (labeled “P”), some of which are heavily faulted (stacking faults are indicated by “SF”), having a size distribution ranging from 20 to several hundreds of nanometers, secondly, fractal-like networks of interconnected nanoparticles (indicated by “F”) having 5–15 nm thick sidearms, and thirdly, small droplet-like 3–5 nm faulted nanoparticles located on the carbon support (labeled “N” and shown at higher magnification in the inset). The presence of 1–2 nm clusters was also revealed by high-angle annular dark field scanning electron microscopy (not shown).

Energy dispersive x-ray spectroscopy (EDXS) allowed for the evaluation of the Cd:Te ratio for nanostructures larger than 10 nm while electron energy-loss spectroscopy (EELS) was used for nanostructures that were 5–10 nm in size. Standardless EDXS and EELS quantification revealed that for all cases analyzed, the Cd to Te ratio was 1 within experimental uncertainty, suggesting that the ablation and deposition of the Cd and Te species were congruent. Selected-area diffraction patterns showed that most of the nanostructures are in the ZB phase with some traces of the WZ phase. Fourier analysis was performed on a number of high-resolution electron micrographs using the WZ reflections that do not overlap with those of the ZB phase (e.g., the {102}WZ reflections). Only in a few cases did some nanoparticles or smaller regions of larger particles exhibit the WZ phase.

Planar defects, having a {111} habit plane, were observed in all of the nanostructures independent of their size. These features are similar to those reported on other CdTe nanostructures or thin films. These stacking faults are believed to accommodate local arrangements of the WZ phase with geometric relationships [111]ZB∥[0001]WZ and [110]ZB∥[1120]WZ, as reported by Yan et al.6

In the second stage of these experiments the CdTe nanoparticles were allowed to accumulate onto a (100) silicon substrate with a native oxide layer to form what is commonly referred to as a cluster assembled film.13,16 Here, instead of Cd–Te species arriving at the substrate’s surface, nanoparticles arrive creating a film with its own unique character. Scanning electron microscopy images of the surface show that the film exists as a loose agglomeration of nanoparticles with poor adherence to the substrate’s surface as is expected for a film formed from the clustering of many small nanoparticles. A θ-2θ x-ray diffraction scan performed on this film gave a few weak peaks barely above the noise level of the measurement.

If instead of a room temperature substrate, the nanoparticles arrive at one that has been heated to 300 °C, there exists enough thermal energy to allow for the nanoparticles to assemble into submicron size grains. A cluster assembled film formed in this manner shows a substantial reduction in porosity. X-ray data (Fig. 2) show that the increased temperature gives rise to prominent diffraction lines, corresponding to both the ZB and WZ phases. Films were deposited over a wide range of temperatures and using a variety of substrates. In all cases, both phases were present. In general, higher temperatures promote the WZ phase. The substrates that showed the strongest tendencies towards the formation of the WZ phase were R-plane sapphire and (100) oxidized silicon.
silicon with the latter showing the most prominent WZ signature. At the same time, it is difficult to determine the exact amount of the WZ phase present in the film as there is a high degree of overlap between the most prominent ZB x-ray peaks and those of the WZ phase. It is further complicated by the fact that the film is textured rather than having randomly oriented grains. Nevertheless, fits to the x-ray data indicate a WZ contribution as high as 40% (Fig. 2).

Photoluminescence (PL) measurements, using a 20 mW HeNe laser, were taken on the CdTe cluster assembled films. The spectra were collected from a spectrometer with a 600 grooves/mm grating and a 512 pixel charge coupled device detector. The films were cooled to 4.5 K using a closed cycle helium refrigerator. The spectra, shown in Fig. 3, exhibit two bound exciton peaks. The lower energy peak at 1.58 eV is likely associated with the ZB phase even though it is slightly redshifted from the 1.596 eV peak normally associated with this phase. The higher energy peak at 1.62 eV likely originates from the hexagonal phase, but it too is redshifted from the 1.654 eV peak observed in the PL spectra of WZ nanoparticles.

The results presented here definitively show the formation of the hexagonal phase in cluster assembled CdTe films deposited using nonconventional PLD processes (deposited at 100 Torr). By depositing CdTe films using conventional PLD techniques (deposited at 10⁻⁵ Torr) Pandey et al. did see a WZ signature in the x-ray diffraction measurements. They suggested that it originated from nanoparticles formed within the plume. For the case of cluster assembled films, nanoparticle formation is enhanced through the suppression of the plume’s expansion by a background gas. Thus, it is not surprising that the cluster assembled films show a WZ signature that is much more convincing in that sharp x-ray lines exist that are clearly distinguishable from those of the ZB phase. The most important aspect of our work, however, is that nanoparticles, through the formation of cluster assembled films, have been used to produce a phase that is metastable in its bulk phase. It is important to realize that the x-ray diffraction data only showed a significant WZ signature if the nanoparticles arrived at the surface of a heated substrate and that higher temperatures promoted the formation of this phase. While the experimental signature that the WZ phase is promoted is clear, it is not obvious what mechanism would promote the metastable phase at elevated temperatures. Some insight is provided through recent direct observations of the sublimation process in CdTe nanoparticles. At elevated temperatures, TEM measurements indicated the transformation of ZB to WZ prior to sublimation. These TEM measurements were carried out at higher temperatures and with much shorter time scales than those used in our growth process. There was also a complication associated with carbon contamination. Despite these differences, the measurements suggest the possibility of an effective transition temperature for phase transformation during film growth. The role of the intermediate nanoparticle formation within this scenario is to enable WZ growth at the elevated temperatures used.

In conclusion, the PLD process has been used in the production of CdTe nanoparticles and cluster assembled films. In both cases, the ZB and WZ phases are observed. When the cluster assembled films are formed through the arrival of nanoparticles at the surface of a heated substrate, it promotes the formation of metastable WZ grains at the expense of the stable ZB phase.

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FIG. 3. Photoluminescence spectra for a cluster assembled CdTe film. The bound exciton peaks at 1.62 and 1.58 eV are assigned to the ZB and WZ phases, respectively.