MODELING OF CDTE EPITAXIAL GROWTH

BY CLOSE SPACED SUBLIMATION

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By

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THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

Department of Physics

UNIVERSITY OF TEXAS AT EL PASO

MAY 2007

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to all my family members: grandparents, uncles and aunts, cousins, brothers and sisters-in-law, nieces and nephews, especially to: Javier, Alicia, Hector and Itzia for giving me the ideal of pursuing higher degrees of education. They have kept track of me in my personal and academic life and have given me strength when I needed it.

Secondly I would like to thank my advisor Dr. David Zubia for letting me live the NanoMIL experience: an exciting and qualified research group where I created new friends and developed new knowledge. Thanks to all old and new NanoMIL members that helped me: Aaron, Cesar, Jacobo, Arev, Mario, Arathi, Shalayna, Sandy, Scott, Brandon, Rafael, Oscar, Miguel, Jose, and Skanda for all the great experiences and moments.

I would also like to express gratitude to the QEM-NSF program for letting me gain experience in characterization methods at The University of Washington under the guidance of Dr. Alex Jen. Thanks to the *Secretaría de Relaciones Internacionales,* which gave me the complementary SEP-SRI scholarship. Finally I would thank the SHPE for the economical support and to the NSF-GK12 fellowship that gave so many good experiences and a financial stability.

To all my friends from the physics department and the ones I left in Mexico City.

To Tara: for her help, support, and patience.

ABSTRACT

A thorough theoretical study of the growth rates of CdTe/Glass thin films using close-spaced sublimation in two limit cases is presented. The approach consists of deriving two equations that calculate the growth rates in the sublimation and diffusion limited cases, respectively. In the sublimation limited scenario, the slowest process is the rate at which the atoms of Cd and Te are being expelled from the source. In the diffusion limited scenario, the slowest process is the transport of Cd and Te atoms from the source to the substrate due to the collisions within atoms.

The model that results from combining both equations predicts a behavior that qualitatively agrees with experimental data. In order to achieve a quantitative fit to experimental data, the model was adjusted using two parameters. The adjustable parameters are loosely associated with losses involved in the evaporation, transport, and condensation mechanisms. When adjusted, the model accurately predicts the growth rate in a temperature range from 400 to 600°C, pressures from 0 to 760 Torr, and substrate-source distances from 0.87 to 1 mm.

The approach used in this study can easily be used to predict growth rates using other substrates and sources by manipulating the adjustable parameters.

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1. INTRODUCTION

1.1. Nano Materials Integration Laboratory

The Nano Materials Integration Laboratory (NanoMIL) at the University of Texas at El Paso (UTEP) focuses on doing research on nanoscale materials and devices. Its area of expertise is patterned polycrystalline solar cells. Recently, NanoMIL began a line of investigation into the epitaxial[1] growth of cadmium telluride (CdTe) and related alloys using the inexpensive close-spaced sublimation (CSS) technique [1]. To facilitate this research, NanoMIL is developing a new rotary, vertical-geometry CSS reactor capable of subliming up to three sources. In preparation for the new line of research, a formal study was conducted to develop deposition conditions that yield smooth, high-quality epitaxial growth of CdTe on CdTe. This study was performed on a traditional horizontal-geometry CSS reactor [2]. The main purpose of the research presented in this thesis is to study the relationship between the deposition conditions and the growth rate. This knowledge will then be implemented in the vertical-geometry reactor.

1.2. CdTe detectors motivation and approach

CdTe-based infrared imaging sensors are used by the military, astronomers and recently in the medical community [3]. For example, pixelated cadmium zinc telluride (CdZnTe) semiconductors are used for X-ray detection in medical and small animal imaging applications. They are also used as room-temperature solid-state gamma ray detectors [4,5]. Another material,

[1] Epitaxy is a kind of interface between a thin film and a substrate. The term epitaxy (Greek; epi "above" and taxis "in ordered manner") describes an ordered crystalline growth on a monocrystalline substrate. Homoepitaxy is a kind of epitaxy performed with only one material. Heteroepitaxy is another kind of epitaxy performed with materials that are different from each other.

$Hg_{1-x}Cd_xTe$ is used for focal plane arrays (FPAs), which require high sensitivity, small pixel size, large-area substrates and low defect density. Mercury cadmium telluride ($Hg_{1-x}Cd_xTe$) has superior electronic and optical properties compared to CdTe, and its bandgap is tunable from 0 to 1.6 eV, depending on the Hg content, which thus provides an unrivalled degree of freedom in infrared (IR) detector design [6].

Although CdTe-based sensors have many important applications, a recurring problem is the lack of low-cost, large-diameter, high-quality CdTe substrates. One approach to this problem is to use silicon wafers since they are low-cost, large-diameter and have ultra-low defect density [7]. However, the use of silicon as a substrate for CdTe introduces the problem of lattice mismatch. The lattice parameter[2] of silicon is 0.543 nm meanwhile the one for CdTe is 0.6482 nm [8]. This difference in lattice parameters results in misfit dislocations in the growth film as the lattices try to adapt to each other. The defects will deleteriously affect electrical properties like mobility [9]. Nevertheless, much research has been performed to develop strategies to reduce the defect density in the CdTe grown on silicon wafers [10].

The world's leading approach to growing high-quality CdTe on silicon is molecular beam epitaxy (MBE) due to its precise control of both chemical composition and thickness. High quality CdTe can be achieved on silicon if it is grown to a thickness of about 6 to 8 microns. However, two problems associated with the MBE technique are its high equipment cost and relatively slow growth rates (typically below 1μm/hr) [7]. The high cost of the equipment (a MBE costs well in excess of one million US dollars) inhibits the number of researchers working

[2] The spacing between a set of atoms periodically repeated in a 3D arrangement in various directions

on this problem. The slow growth rate reduces the pace of technological development since a typical MBE growth of CdTe will last between 6 to 8 hours.

1.3. Contribution of this thesis

Due to the importance of CdTe for IR imaging applications, the high cost of CdTe wafers, the potential for growing high-quality CdTe on silicon, and the high-cost and slow growth rate of MBE; the goal of this research is to provide insight into the growth of CdTe using the close space sublimation (CSS) technique. More narrowly, this thesis focuses on the theoretical modeling of the growth rate of CdTe thin films by CSS. The model presented is based on two processes that limit deposition: sublimation and diffusion. Overall, this thesis reviews different models present in the literature and tests, corrects, and joins two models.

2. LITERATURE REVIEW

2.1. Layers grown by close-spaced sublimation

Studies by McCandless [11], *et al,* at the Institute of Energy Conversion, University of Delaware reported depositions of CdTe over cadmium sulfide (CdS) substrate using close spaced sublimation (CSS). The source temperature range was from 780 ºC to 860ºC. The substrate temperature ranged between 500 ºC and 570ºC showing no effects in the growth rate when varied. The resulting growth rates were in the range of approximately 360-4680 μm/hr. The total thickness of the deposition varied from 1 to 8 μm. Atomic force microscopy (AFM) images shown in the article reveal faceted grain morphology; the tendencies observed were: increasing grain size with increasing substrate temperature for 5 micron thick films, increasing grain size with increasing film thickness for 550ºC substrate temperature, and decreasing grain size with increasing deposition rate.

In other research, de Melo's group [12] reported atomic layer epitaxy (ALE) growth of cadmium selenide (CdSe) films on gallium arsenide (GaAs) substrates using an isothermal close–spaced sublimation system (ICSS) with elemental sources. The target in this system is to create a binary compound when cycling between different elemental sublimation sources. The times of exposure to each source as well as the temperatures of the sources were calculated to reach full monolayer coverage in the substrate for each layer. The CdSe film orientation was reported to be (2 0 0) and (4 0 0) using XRD data. The full width at half maximum (FWHM), which tells the degree of perfection within the crystal, for the CdSe layers grown was 0.0333° or 120 arcsec. When few

cycles between different elemental sublimation sources are made, relatively smooth surfaces are created. The temperatures used in this system were around 300°C [12].

Studies by Alamri [13] experimented on the variables that control the growing rate of CdTe using the close-spaced sublimation technique. The three manipulated variables were: pressure, temperature, and distance from source to substrate. A CdS layer was previously grown over a transparent conductive oxide coated (TCO-coated) glass to serve as substrates for the deposition. The growing conditions were: N_2 as a chamber gas, 700°C for source temperature and substrate temperatures ranging from 480°C to 650°C, the pressures ranged from 10^{-5} Torr to 4.5 Torr, the separation distance spanned from 0 to 11mm. The growth rates ranged from 0 to 80 μm/hr. High growth rates were obtained at high temperatures, small separations, and low pressures. At low temperatures of growth (500 °C) the films showed a (1 1 1) preferred orientation whereas at 530°C, the orientations were (2 2 0) and (3 1 1); no FWHM data was reported.

More interestingly, recent studies by Yan [14] at the National Renewable Energy Laboratory (NREL) revealed material properties of the interface between CdTe grown on CdS, as well as CdTe grown on CdTe, by means of the CSS technique. The characterization was done by means of a high resolution transmission electron microscope (HRTEM) and an energy-dispersive x-ray spectroscopy (EDS) to analyze defects and composition of the layers, respectively. All the growths used the same temperatures: substrate being 550 °C, and source being 640°C. The substrates were hexagonal CdS and cubic CdTe single crystal. Through the CdS-CdTe studies, it is proved that interdiffusion between CdS and CdTe compounds occur, forming $CdS_{1-x}Te_x$

alloys, leading to a concentration of planar defects within the first 0.4 μm of the layer. The CdTe-CdTe depositions also showed a high density of planar defects at the interface.

2.2. CdTe layers grown by molecular beam epitaxy

Molecular beam epitaxy (MBE) is a process involving one or more beams of atoms or molecules that impinge on a crystal or a surface to create an oriented overgrowth of crystalline material [15] under ultrahigh-vacuum conditions (10^{-11} Torr). Single-crystal, multilayer structures with dimensions on the order of atomic layers can be grown using MBE. However, a major drawback for these machines is the high price of the instrument (estimated at millions of dollars) [16].

Yoo reported growing (1 1 1)B CdTe on (1 0 0) oriented silicon by MBE [17]. The thickness of the routinely grown CdTe layers varied from 10 to 20 μm (no rate specified). The films produced were used to detect x-rays, displaying a linear response up to 15eV showing that CdTe is a suitable choice for the detection of x-rays.

Other studies [18] of CdTe (2 1 1)B growths on silicon substrates (2 1 1) reported a near-substrate etch pit density[3] varying from 6×10^8 at 1μm to 1.53×10^5 cm^{-2} at 8 μm of thickness. The etchant agent was hydrofluoric acid (HF) diluted at 2%. From X-ray diffraction (XRD), they observed the presence of twin-free CdTe (2 1 1)B layers: The rocking curve FWHM obtained using this technique ranged from as low as 74 arc-sec (.002°) to 300 arc-sec (.0833°).

[3] Measure for the quality of semiconductor wafers

Giles-Taylor as well, used MBE to grow CdTe layers on GaAs substrates obtaining a maximum deposition rate of 0.72 μm/hr [19]. The temperature of the substrate ranged from 200 °C to 300ºC. The source temperature was 524ºC. The best results were obtained for a substrate temperature of 275ºC. These layers were used for subsequent depositions of CdMnTe. The photoluminescence (PL) spectra displayed a FWHM varying from 10-18 meV. No XRD or electron backscatter diffraction (EBSD) studies were performed on the films.