UNIVERSIDADE FEDERAL DE VIÇOSA
Departamento de Física

RELATÓRIO CIENTÍFICO FINAL
PROJETO FAPEMIG CEX-343/06

AUTOMAÇÃO DE UM SISTEMA DE CRESCIMENTO DE PONTOS QUÂNTICOS DE CdTe

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Sumário

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RESUMO

Este é um projeto de automação do novo sistema de crescimento epitaxial usado na fabricação de pontos quânticos de CdTe. O sistema de crescimento está sendo construído com recursos obtidos junto à FAPEMIG, CNPq e MCT, visando atingir condição de ultra-alto-vácuo e a possibilidade de incorporação de novos elementos. O objetivo principal científico é a investigação da nucleação e dinâmica de crescimento deste sistema, que obedece o modo Volmer-Weber e tem sido muito pouco investigado. As medidas de distribuição e densidade de QDs são feitas no AFM da UFMG, adquirido através do Instituto do Milênio. O estudo teórico da dinâmica de crescimento é feito através da determinação da rugosidade e dimensão fractal, através de análise das imagens de AFM, visando desenvolver modelos de automato celular, que permitam reproduzir os dados experimentais.

Palavras chave:

CdTe, nanoestruturas, automação, pontos quânticos, crescimento epitaxial
Introdução

Este relatório se refere ao processo CEX343/06 iniciado em 01/12/2006 e finalizado em 15/04/2008 com recursos liberados no valor total de R$14.901,68.

Do ponto de vista científico, este trabalho objetiva continuar o estudo do crescimento de pontos quânticos de CdTe sobre substratos de Si, utilizando o novo sistema de crescimento de epitaxia por paredes quentes, desenvolvido ao longo dos últimos dois anos. Pretende-se continuar os estudos sobre o processo de nucleação e a dinâmica de crescimento dos pontos quânticos de CdTe, através da análise de imagens obtidas por microscopia de força atômica e a caracterização estrutural utilizando difração de raios-x. Do ponto de vista tecnológico, esta proposta visa desenvolver um sistema de automação dos obturadores e controladores de temperatura do novo sistema de crescimento montado através do projeto CNPq-475455/2004-5, que se encerrou em julho-2007.

Resultados

A figura 1 mostra foto do novo sistema completo, incluindo a câmara de introdução e o sistema de transferência. A câmara de vácuo foi testada e certificada para operação em pressões inferiores a $10^{-9}$ Torr. Foram projetadas e construídas novas células de efusão que permitem operação em temperaturas até 1000 °C. A figura 2 mostra foto de uma das células construídas. O sistema permite a utilização de até 7 células ao mesmo tempo. Inicialmente, foram colocadas em operação 4 células, contendo os elementos Te, Zn, Mn e o composto CdTe, respectivamente.
Fig. 1 – Foto da câmara de vácuo do sistema MBE.

Fig. 2 – Foto da célula de efusão construída durante o projeto.

Foi projetado e construído novo sistema de controle de temperatura que permite o controle automatizado das temperaturas de evaporação de cada uma das células. Finalmente, construímos também, o sistema para acionamento dos obturadores para cada uma das células de efusão. A movimentação dos obturadores é feita utilizando-se aletas rotativas acionadas por ar comprimido. A direção do fluxo de ar (direção de movimento) é controlada por válvulas solenóides. O sistema foi
projetado para permitir tanto o acionamento manual quanto automatizado, através do computador. A figura 3 mostra o “rack” de controle montado ao lado do computador. Todos os sistemas, com exceção do responsável pela medida do vácuo, foram desenvolvidos e montados no Laboratório por uma equipe que contou com dois estudantes de mestrado (Jefferson Suela, tese concluída em 2007, e Joaquim Pinto Gomes) e dois bolsistas de iniciação científica (Fábio Santos Nascimento, PIBIC e Octávio Gregio de Araújo, deste projeto).

![Fig. 3 – Foto do rack de controle do sistema, mostrando o sistema de medida de vácuo (a), o sistema de controle de temperatura (b), controle de potência (c) e controle dos obturadores (d) ao lado do computador de controle.](image)

Novas amostras de pontos quânticos de CdTe foram crescidas sobre Si(111) e caracterizadas por AFM e difração de raios-x. As medidas de AFM foram feitas em
cooperação com o Laboratório de Nanoscopia da UFMG dentro do projeto Instituto do Milênio de Nanociências. As medidas de difração de raios-x foram feitas no Laboratório Nacional de Luz Sincroton. Utilizamos medidas de difração coplanar assim como difração com incidência rasante, para caracterização estrutural das amostras.

As medidas de raios-x permitiram determinar as dimensões laterais e verticais das ilhas e sua razão de aspecto, assim como a mosaicidade. Estes dados são mostrados na tabela abaixo:

<table>
<thead>
<tr>
<th>Amostra</th>
<th>H (Å)</th>
<th>L (Å)</th>
<th>M (graus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>160 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>189 ± 2</td>
<td>258 ± 3</td>
<td>7,3 ± 0,5</td>
</tr>
<tr>
<td>C</td>
<td>378 ± 7</td>
<td>264 ± 3</td>
<td>4,8 ± 0,5</td>
</tr>
<tr>
<td>D</td>
<td>473 ± 11</td>
<td>306 ± 4</td>
<td>3,9 ± 0,5</td>
</tr>
</tbody>
</table>

Tabela 1: Comparação entre as dimensões médias dos pontos quânticos na direção vertical (H) e na direção horizontal (L) e a mosaicidade (M).

Do ponto de vista teórico, o modelo de crescimento em uma dimensão foi estendido para o caso real, com substrato em duas dimensões. Esse trabalho está sendo desenvolvido pela estudante de Mestrado Tatiana Estorani de Faria, cuja defesa de tese está prevista para junho de 2008. O modelo considera os seguintes mecanismos básicos: deposição, difusão e evaporação controladas por ativação térmica associadas com diferentes regras de dissociação para partículas sobre o substrato original de Si e partículas sobre partes do filme cobertas por
CdTe. Devido à simetria do substrato de Si(111), o modelo foi implementado em uma rede triangular. Um dos padrões de crescimento é mostrado na figura 4. As estatísticas sobre distribuição de altura e largura dos pontos quânticos estão em fase de simulação.

![Fig. 4 - Padrão de crescimento obtido pelo modelo em duas dimensões.](image)

Além das simulações em duas dimensões desenvolvemos uma análise de tempos longos do modelo unidimensional. O principal resultado foi a identificação de diferentes regimes de escala dentro e fora dos platôs, indicando assim um novo expoente na caracterização da classe de universalidade do crescimento dessas interfaces.

Em paralelo, foi desenvolvido, também, um modelo para descrever recentes experimentos de deposição de CdTe sobre substratos de vidro cobertos por óxido

![Gráfico 5 - Perfis de rugosidade em função da temperatura de crescimento.](image)

Além disso, iniciamos também o crescimento de pontos quânticos de CdTe sobre substratos de BaF₂. O BaF₂ é transparente desde comprimentos na faixa do ultra-violeta até o infra-vermelho, o que permite a caracterização ótica dos pontos
quânticos obtidos de uma maneira muito mais fácil do que quando crescidos sobre sílice.

**PRODUÇÃO CIENTÍFICA**


O projeto propicia ainda a formação de 4 alunos de iniciação científica (um deles com bolsa custeada pelo projeto e os outros 3, com bolsas PIBIC-FAPEMIG e PIBIC-CNPq. Um aluno de mestrado defendeu sua dissertação em março de 2007, outro está com defesa de dissertação marcada para o dia 15/05/2008 e outros dois deverão apresentar a dissertação até julho de 2008.

Desta forma, podemos concluir que o projeto foi realizado com sucesso, cumprindo com todos os objetivos propostos, além das expectativas iniciais.

Além disso, com a aprovação do remanejamento de recursos solicitado e a prorrogação do prazo de execução do projeto, foi possível a aquisição de um espectrofotômetro que está sendo utilizado na caracterização de pontos quânticos coloidais, produzidos em colaboração com o Departamento de Química da UFV.
Esta é uma nova área de pesquisa, que já apresenta resultados que serão apresentados na forma de painel no XXXI Encontro Nacional de Física a Matéria Condensada, de 05 a 09 de maio de 2008 em Águas de Lindóia.

A figura 6 mostra o espectro de fotoluminescência, medido utilizando-se o novo equipamento, para as 3 amostras de pontos quânticos mostradas na foto da figura 7.

![Figura 6 - Fluorescência das amostras da figura 4. O pico em 370 nm é devido à radiação ultravioleta usada para excitar as amostras.](image)

![Figura 7 - Amostras de pontos quânticos de CdS.](image)
Atividades executadas pelo bolsista

- Adequação das instalações elétricas do laboratório de Epitaxia
- Projeto e implementação do módulo de controle de obturadores
- Projeto e implementação do módulo de potência para as células de efusão
- Desenvolvimento do software de controle usando a plataforma LABVIEW

As figuras a seguir mostram alguns dos circuitos projetados e construídos para a implementação do sistema de controle, além da tela principal do software desenvolvido.

Figura 8 – Circuito de chaveamento da potência entregue à carga

Figura 9 – Esquema da placa de acionamento dos fornos
Figura 10 – Diagrama de blocos contendo código gráfico do programa desenvolvido em LabView

Figura 11 – Painel frontal do programa desenvolvido em LabView
Figura 12 – Sistema MBE construído

Avaliação do bolsista

O Bolsista executou todas as tarefas que estavam previstas no projeto inicial, com habilidade e iniciativa, portanto, seu desempenho foi excelente.
Low temperature growth of high quality CdTe polycrystalline layers

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Abstract
We have investigated the growth of CdTe thin films on glass substrates by hot wall epitaxy. The layers have been characterized by scanning electron microscopy, atomic force microscopy, profilometry, x-ray diffraction and optical transmission. The grown samples are polycrystalline with a high preference for [1 1 1] orientation. Atomic force microscopy and scanning electron microscopy reveal pyramidal grain shapes with a size of around 0.3 μm. The surface roughness increases with sample thickness and growth temperature, reaching about 700 nm for 10μm thick layers grown at 300°C. Samples with a thickness of 2 μm grown at 150°C showed a roughness of less than 40 nm. Optical transmission measurements demonstrate layers with high optical quality.

1. Introduction

CdTe is one of the most important candidates for thin film solar cell production and has been studied intensively in recent years [11]. Various techniques have been investigated for the production of CdTe thin films: screen printing [2], electro-deposition [3], vacuum evaporation [4], chemical vapour deposition [7] and molecular beam epitaxy [8], all having their advantages and disadvantages. Up to now, the most efficient cells, with efficiency of about 16%, have been produced using the chemical vapour deposition and processing temperatures between 500 and 650°C [9]. However, the use of lower processing temperatures is advantageous if pre-processed substrates are used. The reduction of growth temperature below 300°C would make the CdCl₂ activation process the limiting factor [10] for temperature sensitive substrate materials. Another advantage of low processing temperatures is the production of hybrid x-ray detector arrays of CdTe on silicon substrates already containing the electronics, which have been produced up to now using the bump bond technique [11-13]. Besides that, low temperature processing can be even necessary in the case of using alternative transparent conductive oxide contact layers or if hybrid structures with polymer substrates are the objective [6, 14]. In this work, we investigate the use of hot wall epitaxy (HWE) for the growth of polycrystalline CdTe layers on glass substrates. Thin films with thickness in the range 0.2-10μm were produced and characterized by electron scanning microscopy, atomic force microscopy, profilometry, x-ray diffraction and optical transmission in the visible and near infrared. Our results show that high quality layers can be grown at temperatures as low as 150°C.

2. Experimental

HWE is a well-established technique able to produce very high quality epitaxial semiconductor films on many crystalline substrates such as silicon, gallium arsenide and indium phosphide [15-17]. However, to our knowledge there is no report on its use with amorphous substrates. In this work, we have used 0.3 mm thick glass slides as substrates. The 9 x 9 mm substrates were degreased with acetone, truly washed in distilled water and gently etched for 2 min in a 3% HF solution.

The HWE growth system used consists of a two furnace system, for source and substrate, separated by a shutter. The deposition occurs at pressures between 3 x 10⁻⁶ and 4 x 10⁻⁴ Torr, obtained by a diffusion pump system. The source temperature can be controlled in the range between 500 and 590°C, producing growth rates between 0.01 and 5 Å s⁻¹. The growth time can be controlled from some minutes up to many hours, corresponding to sample thickness from...
10 Å to 15 μm, depending on source temperature. In this study we investigate samples grown at the same growth rate, varying the growth time from 15 to 450 min, which corresponds to thicknesses between 0.15 and 10 μm. The substrate temperature was varied between 150 and 500 °C. High purity commercial C60 (99.999%) was used as source material.

The film thickness has been measured using a stylus profiler (AMBROS XPI). Almost no influence of substrate temperature on the growth rate has been observed in the investigated range. The thickness was obtained averaging at least eight measurements around the sample perimeter. The thickness uniformity was better than 5% for all samples. The stylus profiler was also used to measure the surface roughness as a function of growth time and temperature. The critical exponents were determined, using dynamic scaling theory, in order to obtain information about the growth dynamics. Sample morphology was investigated using scanning electron microscopy (LEO model 435 VP) and atomic force microscopy using a NTEGRA SOLVER scanning probe microscope, operating in the intermittent contact mode. A DIANA diffractometer was used to investigate the structural properties of the grown layers by x-ray diffraction. Two 2θ scans were obtained using the Bragg-Brentano geometry and Cu target. Optical transmission and reflection were measured using a Perkin Elmer 1000 Fourier Transform spectrometer to determine the optical absorption in the range from 0.8 to 1.6 eV.

3. Results and discussion

The scanning electron micrograph reveals a grain size which varies slowly from about 0.2 μm for 0.25 μm thick samples to about 1.5 μm for samples with thickness above 5 μm. Figure 1(a) shows a scanning electron micrograph of a 2.5 μm thick sample taken at 15 kV with a 10000 magnification. On can clearly see that grain size distribution is very uniform. Details of sample morphology investigated by atomic force microscopy can be observed in figure 1(b), which shows a 2 μm x 2 μm APM image of a 2.5 μm thick sample. The image clearly reveals the grain’s pyramidal shape with a base width of approximately 0.5 μm.

The x-ray diffraction measurements have revealed that all grown films with thicknesses of above 1 μm, exhibited only the (1 1 1), (2 2 0), and (4 4 4) diffraction peaks, indicating highly textured samples with a preferred [1 1 1] growth orientation. The only factor affecting the film texture was layer thickness. This can be observed in figure 2, which shows the diffraction spectra for two samples grown under the same conditions (growth rate and substrate temperature) but with different thicknesses. The diffusion pattern in figure 2(a), for a 0.25 μm film, shows the (2 2 0), (1 1 1) and (3 3 3) peaks, as expected for a polytetrahedral sample, while in the pattern shown in figure 2(b), obtained for a 1.5 μm thick layer, one can observe only the (1 1 1) and (3 3 3) peaks, indicating a highly textured layer. This result indicates that the growth process initiates by the nucleation of islands with all possible orientations, but as the growth proceeds, the [1 1 1] orientation dominates and after the deposition of about 1 μm most of the grains have this orientation. This behavior has already been observed for C60 layers obtained by other growth techniques, almost independent of substrate material, but in most cases this was observed only for high substrate temperatures, usually above 500 °C [18]. We have not observed any influence of the substrate temperature in the diffraction spectra of our samples in the investigated range 150-300 °C. The preparation of such highly oriented films at temperatures as low as 150 °C is an advantage of the HWA technique, which has not been reported before.

Using surface profiles obtained with the stylus profiler we have evaluated the sample roughness, determined the root mean square fluctuation of surface height over a specified length scale, and determined the critical exponents α and β for our samples. The roughness (or Hurst) exponent α and the growth exponent β are recognized as important tools to understand the deposition process and the growth
properties of thin films [19]. Details of determination of $\sigma$ and $\beta$ for these CdTe layers have already been published elsewhere [20]. Figure 3(a) shows the surface roughness as a function of growth time for samples grown at 150°C. This time dependence can be used to evaluate $\beta$, equal to 0.39 ± 0.08, by fitting a power law ($\sigma \sim \beta^\beta$). For each sample, the roughness has also a power law dependence with length scale ($r$), which can be used to determine $\sigma$ ($\sigma \sim r^\alpha$). This behaviour indicates that the CdTe surface has a self-affine character. Figure 3(b) illustrates the determination of $\alpha = 0.67 ± 0.03$, for a sample with growth time equal to 120 min and a substrate temperature of 290°C. The value of $\alpha$, measured as a function of sample thickness, is almost constant and is very close to the one predicted by the non-linear MBW growth theory [19] and can be associated with 3D island growth mode [21, 22].

We have observed a very strong dependence of the surface roughness of these layers on growth temperature. However, the observed behaviour is not the one typically expected or predicted by temperature activated growth models, where the increase in temperature should produce smoother surfaces [23]. The roughness of our samples increases with temperature, as can be seen in figure 4. A similar behaviour has been observed, recently by Elsholz et al [24], for oxide films grown by magnetron sputtering. A detailed study of the effect of growth temperature on the critical exponents of CdTe films grown by HWC has been published elsewhere [25].

Finally, we have investigated the optical quality of the grown layers. As shown in figure 5, the optical transmission spectra at room temperature were recorded between 0.8 and 1.6 eV. At low energy side, in the transparent region of CdTe, these transmission spectra show interference fringes due to multiple reflection of light at the sample surface and the CdTe/glass interface. The sample thickness is evaluated from the two adjacent minima (or maxima) of the transmission spectra using the relation $d = (n_1n_2)/(n_2\lambda_1 - n_1\lambda_2)$ where $n_1$ and $n_2$ are the index of refraction [26] at $\lambda_1$ and $\lambda_2$, respectively. From this thickness and the transmission spectra, corrected for the refraction, the absorption spectra $\alpha_{av}(hv)$ was evaluated using Beer–Lambert's law. In the inset of figure 5 the square
Figure 5. Room temperature optical transmission spectra of 5.9 μm thick CdTe on glass substrate. Inset: plot of square of the absorption coefficient times photon energy, (αhν)^2, against the photon energy, hν, extrapolated intercept at 1.519 eV.

of the absorption coefficient times photon energy, (αhν)^2, is plotted against the photon energy, hν, to obtain the band gap from the extrapolated intercept, assuming a direct band gap. The reasonably straight line obtained indicates that the assumption of a direct band gap is correct and the energy at the intercept was found to be 1.519 eV. This value has to be corrected by 9 meV due to exciton binding energy in order to obtain the true optical gap E_g, which results to be 1.528 eV, which coincides with the value reported in the literature for bulk CdTe at 300 K [27].

4. Conclusions

CdTe polycrystalline thin films were grown using the HWE technique on glass substrates. All samples produced are highly textured, with preferential orientation in the [1 1 1] direction. The degree of preferential orientation increases with layer thickness and for samples thicker than 5 μm no other diffraction peak is observed besides the [1 1 1] family. The calculated values of the critical exponents indicate 3D island growth mode. Our results show that roughness increases with growth temperature, a behaviour which is the opposite of that usually expected and indicate the necessity of a detailed study of the effect of temperature. Pronounced interference fringes and a steep onset of the fundamental absorption with direct band gap energy at 1.528 eV, in the transmission spectra, are indications that CdTe layers grown by HWE on amorphous glass substrate have a very good optical quality. The most important result is that high quality and oriented layers were obtained at a very low growth temperature of 150°C. Such a low processing temperature opens the possibility for the growth on preprocessed substrates already containing electronic circuits and even on polymer substrates, for the production of hybrid cells.

Acknowledgments

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References

Study of thermal and optical properties of the semiconductor CdTe by photopyroelectric spectroscopy

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In this study, photopyroelectric spectroscopy (PPES) was used to obtain thermal and optical properties of CdTe thin films in the 300–1200 nm wavelength range. The samples studied were grown on glass or BaF2 substrates using the hot wall epitaxy technique with varying thicknesses. The normalized photopyroelectric signal intensity and its phase were independently measured as a function of wavelength λ and chopping frequency f. Equations of both the intensity and the phase of the PPES signal, taking into account the thermal and the optical characteristics of the pyroelectric detector, were used to fit the experimental results. From the fittings, we have obtained the values of thermal diffusivity coefficient α, thermal conductivity k, optical absorption coefficient, and the optical gap of CdTe. © 2007 American Institute of Physics [DOI: 10.1063/1.2734940]

I. INTRODUCTION

The photopyroelectric spectroscopy presents great utility for obtaining thermal parameters of solid materials, such as thermal diffusivity, thermal conductivity, and specific heat. Also, optical parameters, such as optical absorption coefficient, quantum efficiency of nonradiative transitions, and optical gap, can be determined. Among the various physical parameters which can be measured, the thermal diffusivity is particularly important because as the optical absorption coefficient, it is unique for each material and allows us to obtain the thermal conductivity and specific heat. Furthermore, the determination of the thermal conductivity is important to study the heat transfer processes by plasmons and by carriers (electrons or holes). In this study, we investigated thin film samples of cadmium telluride (CdTe) grown on BaF2 (barium fluoride) or glass substrates using the hot wall epitaxy (HWE) technique. CdTe is a semiconductor composite of the group II–VI with a lattice constant of 6.4 Å, and an energy gap of 1.4–1.5 eV. CdTe is recognized as a very attractive material for the fabrication of low cost and high-efficient electronic devices such as solar cells, gamma and x-ray room-temperature nuclear detectors, and electro-optic modulators. Another photothermal technique, the photocoustic spectroscopy, has already been used for studies in CdTe mainly related to measurements of surface velocities and bulk recombination time. Here photopyroelectric spectroscopy (PPES) was used to obtain the thermal and optical properties of CdTe in the 300 < λ < 1200 nm wavelength range. The normalized photopyroelectric signal intensity as a function of the wavelength V(λ) and its phase F(λ) were independently measured, as well as the intensity as a function of the chopping frequency V(f) and its phase F(f), for a wavelength on the saturation part of the PPES spectrum. Equations of both the intensity and the phase of the PPES signal, taking into account the thermal and the optical characteristics of the pyroelectric (PVDF) detector, were used to fit the experimental results. From the fitting of the graph F(λ) vs λ, we obtained the value of the thermal diffusivity coefficient α. Fitting the graph V(f) vs f allows the determination of the thermal conductivity k. And finally, from the fittings of the graphs V(λ) vs λ and F(λ) vs λ, we obtained the optical absorption coefficient β and the optical gap of the CdTe samples.

II. EXPERIMENTAL METHODOLOGY

A. The photothermal spectrometer

The photothermal spectrometer shown in Fig. 1, is composed by a monochromator (Scientech model 90551), a mechanical slotted wheel chopper (Stanford Research System SR 540), and a 450 W xenon lamp (Thermo Orion) or a 7 mW He-Ne laser (Coherent model 31-2074) used as excitation sources for wavelength scanning or frequency scanning, respectively. The homemade photothermal chamber can be attached directly to the exit slit of the monochromator or through an optical cable in place of the mirror, shown in the figure. The measuring system was composed by a lock-in amplifier (Stanford Research System SR 530) locked at the chopper frequency. Data were acquired automatically and the system was controlled by a computer via a general purpose interface bus interface.

![Fig. 1. Schematic of the experimental setup used for photothermal spectroscopy measurements of CdTe samples. Illumination and acquisition were synchronized using a lock-in amplification arrangement.](Image)
B. The photopyroelectric cell

The homemade PPE chamber was designed to improve the signal to noise ratio and construct at The Federal University of Viçosa. The cell was setup with the CdTe layer in contact with the pyroelectric detector. This one was a 40 µm-thick β-polymethylacrylate film with aluminum electrodes evaporated on both surfaces for electrical contacts, one of which was painted with a very thin layer of black ink and was in direct contact with the sample. The values for the thermal and electrical parameters of PVDF at room temperature (as provided by the manufacturer) are 3.0×10⁻³ C/m² K for the pyroelectric coefficient, 12 for the relative dielectric constant, 5.4×10⁻⁸ m²/s for the thermal diffusivity, and 0.13 W/m K for the thermal conductivity. The heat generated by the absorption of the chopped probe produces the voltage in the pyroelectric detector and the signal is measured by the lock-in amplifier.

C. Sample preparation

The samples studied in this work were grown using the LWE technique, which is a very simple growth technique, used for the growth of compounds which evaporates congruently. It has already proved to produce very high quality CdTe epitaxial layers in different substrate materials. The growth system used consists of two independently controlled furnaces, used for source and substrate, and a shutter, placed within the 1 cm gap between the two furnaces, which controls the beginning and the end of the growth process. The growth system was installed inside a Pyrex chamber and maintained at a pressure of about 5×10⁻⁷ Torr during the whole growth process. The growth can be controlled from 0.01 to 5 A/s. In this work, the source furnace, containing polycrystalline CdTe (99.9999%), was maintained at 530 °C and the substrate temperature was between 150 and 350 °C, resulting in a growth rate almost independent of substrate temperature and equal to 1.4 A/s. The substrates were degreased, dipped in a 2% HF solution for 2 min, and thoroughly rinsed in de-ionized water just before the introduction in the growth system. The deposition times used varied from 30 to 450 min, resulting in film thickness between 0.855 and 15.6 µm, as determined by a stylus profiler.

III. MANDELIS–ZVER THEORETICAL MODEL (PPES)

The modulated light intensity which excites the sample obeys the expression

\[ I = I_a \left( 1 + \cos(\omega t) \right) \]

where \( I_a \) is the amplitude of the beam intensity and \( \omega(=2\pi f) \) is the angular chopping frequency. The absorption of this modulated pulsed light gives rise to a periodic heating of the sample owing to nonradiative relaxation of excited states. The nonradiative conversion efficiency \( \eta(\lambda) \) is considered near unity, since luminescence effects in CdTe have very low efficiency in the wavelength range used in this study. The generated heat is detected by a pyroelectric detector which is in direct contact with the sample.

The detected signal \( V(\omega, t) \) is proportional to the pyroelectric coefficient \( p \) of the detector and to the temperature distribution along the detector thickness \( T_p(x, t) \)

\[ V(\omega, t) = \left[ \frac{p}{K \varepsilon_r} \right] \int T_p(x, t) \, dx \]

where \( T_p \) is the detector thickness, \( T_p(x, t) \) is the temperature field in the bulk of the detector, \( K \) is the relative dielectric constant of the material, \( \varepsilon_r = \varepsilon - 1 \), and \( \varepsilon_r \) is the vacuum dielectric permittivity. The heat propagation across the whole chamber is governed by heat diffusion equations of each medium coupled via boundary conditions at the interfaces \( T_a = T_i \) and \( k_d \partial T_d \partial x = k_p \partial T_p \partial x \), where \( a \) and \( p \) representing consecutive media, as established by Mandelis and Zver. The signal \( V(\omega, t) \) obtained by integrating the diffusion equations is normalized by the ratio \( V(\omega, t)/V_{PPS} \) where \( V_{PPS} \) is the signal measured directly over the detector painted with a very thin

![Image 1](image1.png)

**FIG. 2.** Experimental points (dots) and the line of the best fit for the PPE normalized phase of the CdTe film on a glass substrate as a function of the chopping frequency of the input He-Ne laser at 632.8 nm.

![Image 2](image2.png)

**FIG. 3.** Experimental points (dots) and the line of the best fit [Eq. (4)] for the PPE normalized voltage of the CdTe film on a glass substrate as a function of the chopping frequency of the input He-Ne laser at 632.8 nm.
layer of a black ink. In this latter case the detector is considered thermally thick and optically opaque, i.e., $\mu_p < L_p$ and $\beta_p < L_p$, where $\mu_p = (\alpha_p / \pi f)^{1/2}$ is the thermal diffusion length of the detector, and $\beta_p$ is its optical absorption length. Thus, $\exp(-\sigma_g z) \approx 1,$ $\sigma_g \ll 1,$ and $\eta_g = 1,$ where $\sigma_g = \beta_p / \alpha_p$ and $\alpha_p = (1 + \eta_g \alpha_p) \alpha_p = c_0 f / \alpha_p$ (n-g, s, p, that is, g-gas, s-sample, p-pyroelectric). Then, the normalized voltage signal results in [5, 9, 12]~

\[
V_s(\beta_n, \alpha) = \left( \frac{\eta_s \tau_s}{\tau_s - 1} \right) \left\{ (b_{ps} + 1)(b_{ps} + 1) e^{\alpha_p z} + (b_{ps} - 1)(b_{ps} - 1) e^{-\alpha_p z} \right\} \times \left[ \frac{b_{ps} + b_{ps}}{b_{ps} + 1}(b_{ps} + 1) e^{\alpha_p z} - (b_{ps} - 1)(b_{ps} - 1) e^{-\alpha_p z} \right],
\]

where $b_{ps} = k_p / \alpha_p$ and $L_S$ is the sample thickness. Equation (3) is a complex function of the thermal, optical, and geometrical parameters of the system, and governs our results since we worked at shorter frequencies above the maximum required for its validation ($\mu_p < L_p$, which means frequencies above 10.7 Hz). Assuming the case where the sample is in an optically opaque condition, that is, in the saturated region of the spectra, then the normalized voltage signal results in [2, 3, 11, 12]~

\[
V_s(\alpha) = 2 \eta_s \frac{(b_{ps} + b_{ps})}{(b_{ps} + 1)(b_{ps} + 1) e^{\alpha_p z} - (b_{ps} - 1)(b_{ps} - 1) e^{-\alpha_p z}}
\]

and the corresponding phase equation $\phi_s(\alpha)$ (Refs. 2, 8, 11, and 12)

\[
\phi_s(\alpha) = -\arctan \left( \frac{(b_{ps} + b_{ps}) \cosh(\alpha_p z) + (b_{ps} + b_{ps}) \sinh(\alpha_p z)}{(b_{ps} + 1) \cosh(\alpha_p z) + (b_{ps} + b_{ps}) \sinh(\alpha_p z)} \tan(\alpha_p z) \right).
\]

Equations (4) and (5) are complex and real functions, respectively, and are used to obtain the thermal parameters: thermal diffusivity $\alpha$ and thermal conductivity $k$. In our frequency scanning measurements, the laser beam size was about 1.02 mm with a beam divergence 0.79 mrad, and during the wavelength scanning experiment, we have used a beam collimator of 2 mm diameter for the exit slit of the monochromator. These dimensions are at least one order of magnitude higher than the thermal diffusion length of bulk CdTe, and they are much smaller than the two lateral dimensions of the sample, photothermal cell, and detector justifying the use of this one-dimensional model.

IV. RESULTS AND DISCUSSION

Figures 2 and 3 show, respectively, the normalized phase $\phi_s(\alpha)$ and voltage amplitude $V_s(\alpha)$ as a function of the chopping frequency, for the CdTe film on a glass substrate. The film thickness was 3.42 $\mu$m (sample 2 in Table 1). The data were recorded in the saturated region of the PPE spectra, for the case where the detector is far from the thick-to-thin transition, that is, above 160 Hz. The power source was the He-Ne laser (centered at 632.8 nm). For all samples, the experimental points for the normalized phase obey a linear dependence on the square root of the frequency for frequencies below 1400 Hz (see Fig. 2). This means that the fractional term that precedes $\tan(\alpha_p z)$ in Eq. (5) is approximately unity in this frequency range. In fact, this function differs from unity by less than 6.7% in that frequency range when we consider appropriate values for thermal conductivity and diffusivity coefficients. This permits us to approximate Eq. (5) to the simple relation $\phi_s = -\alpha_p z$. Therefore, the thermal diffusivity $\alpha_p$ is directly obtained from the slope of the fitting curve $\phi_s$ vs $f^{1/2}$ (the continuous line of Fig. 2), using the relation $\alpha_p = (\pi f / \alpha_p)^{1/2}$. Values obtained from this analysis are shown in Table 1.

The $\alpha_p$ values of Table 1 were, then, used for the $V_s(\alpha)$ fitting utilizing Eq. (4), and the thermal conductivity $k$ became the single adjusted parameter of the results shown in Fig. 3. Table 1 also shows physical parameters for other CdTe samples. The main result is an increase of both thermal diffusivity and thermal conductivity with sample thickness, with the value obtained for thicker samples being closer to the expected value. This behavior has already been observed before by Alvarado-Gil et al. and Gonzalez-T et al., who have measured the thermal diffusivity of CdTe polycrystalline films on glass substrates using open-cell photonicoustic technique. In a general way, the thermal diffusivity increases as the film thickness increases, which is in agreement with the fact that the thermal diffusivity of polycrystalline CdTe is $5.5 \times 10^{-9}$ m$^2$/s. Another explanation for this behavior may be the presence of a larger amount of

<table>
<thead>
<tr>
<th>Sample</th>
<th>CdTe film on glass plate (sample 1)</th>
<th>CdTe film on glass plate (sample 2)</th>
<th>CdTe film on BaF$_2$ plate (sample 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_s$ ($\mu$m)</td>
<td>0.855</td>
<td>3.42</td>
<td>7.0</td>
</tr>
<tr>
<td>$\alpha$ (m$^2$/s)</td>
<td>$7.32 \times 10^{-10}$</td>
<td>$8.79 \times 10^{-9}$</td>
<td>$1.07 \times 10^{-8}$</td>
</tr>
<tr>
<td>$k$ (W/m K)</td>
<td>0.139</td>
<td>0.595</td>
<td>2.23</td>
</tr>
</tbody>
</table>

---

[Note: The table is not fully visible due to the cropped text, but it is assumed to continue as shown above.]
The correlation coefficient is 0.99418 and $\chi^2$ is 0.00117.

FIG. 4. PPE $V_n$ spectrum as a function of wavelength for the CdTe film on a BaF$_2$ substrate at 100 Hz chopping frequency. The dots represent experimental results and the full line represents the fit (Eq. (3)).

Defects in the thinner samples, Rodriguez et al. [27] have studied the influence of inclusions and precipitates on the thermal properties of CdTe single crystals and observed that the diffusivity is higher for "high-quality single crystals" and strongly depends on the types of defects observed.

Figure 4 shows the experimental PPE $V_n$ spectrum (dots) and the fit (full line) of CdTe film on a BaF$_2$ substrate between 300 and 1200 nm for 100 Hz chopping frequency. The spectrum presented a transmission-like behavior due to the inverted absorption band. The continuous line fitted to the PPE spectrum of Fig. 4 were obtained from Eq. (3), obeying the thermally thick and optically opaque conditions of the pyroelectric detector. The absorption $\beta_3(\lambda)$ function was represented by one Gaussian function centered at 550 nm. The thermal quantities $\alpha_0$ and $\beta_3$ obtained previously were used as fixed parameters here and the adjusted values were the intensity, the linewidth, and the center of the Gaussian function. Figure 5 shows the corresponding PPE $F_n$ spectrum. We believe the variation of the phase in the above band gap region of CdTe, i.e., between 300 and 800 nm in Fig. 5, is due to low crystalline quality of our samples which could have the presence of Te aggregates. [27] We know that the normalized phase signal is much more sensitive to those "impurities" than the normalized intensity of the signal since the normalized photopyroelectric signal is very small in the above band gap region. Hence, the signal $V_n$ in Fig. 4 presents the same features of Fig. 5 but in a lesser degree, as we can see in both figures.

From the shoulder of the spectra of Fig. 4 and 5, we can obtain the optical gap of the CdTe film. Figure 6 shows the PPE $V_n$ signal plotted as a function of photon energy, giving the value 1.53 eV for the optical gap. This value is in excellent agreement with that of the literature (value in the range 1.4–1.5 eV). [16,19]

Figure 7 shows the optical absorption coefficient $\beta$ obtained from the $V_n$ spectrum of Fig. 4 solving Eq. (3) numerically. According to this result, we conclude that the CdTe sample is opaque, i.e., $\beta^{-1}<\lambda_0$ in the wavelength region below 850 nm, but the signal saturates only for the wavelengths below 812 nm, which corresponds to the optical gap.

FIG. 5. PPE $F_n$ spectrum as a function of wavelength of the CdTe film on a BaF$_2$ at 100 Hz chopping frequency.

FIG. 6. PPE $V_n$ spectrum as a function of photon energy, corresponding to Fig. 4.

FIG. 7. Optical absorption coefficient spectrum for the CdTe sample obtained from the $V_n$ spectrum of Fig. 4 using Eq. (3) (resolved for $\beta$ numerically).
in this CdTe sample. Figure 8 shows $\beta$ plotted in energy space and the optical gap can clearly be seen at 1.53 eV. Also the intensity of the Gaussian curve depicted in Fig. 4 is of the same order of magnitude of the optical absorption coefficient in the saturated region of Figs. 7 and 8 and this order of magnitude agrees very well with that of the literature (value in the range $-10^5$--$10^7$ m$^{-1}$).

V. CONCLUSIONS

The data of Table I show great variation for CdTe physical parameters with the thickness of the samples. Our value of thermal diffusivity for the thickest sample differs from that given by the literature (value $3.95 \times 10^{-9}$ m$^2$/s for 42 $\mu$m CdTe) by 24%. Likewise, the thermal conductivity difference for the 7.8 $\mu$m sample was 39% (literature value 3.63 W/m K). We believe that these differences can be explained by variations in the production process leading to structural and orientational differences between films. As already pointed out in the literature, the value of the thermal diffusivity and conductivity of CdTe strongly depends on the presence of defects. The defect density is expected to be higher in the thinner samples. Besides that, another possible reason for this behavior could be the change in sample density with thickness, which is sometimes observed for evaporated polycrystalline films.

The PPES technique showed to be of great utility to obtain thermal and optical properties of these semiconductor films. We believe that our measurements of the spectral dependence of $\beta$ in the 300–1200 nm wavelength range are the first reported for CdTe using PPES technique. These data will undoubtedly assist in on-going efforts to understand physics of this important class of semiconductors.

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