CHARACTERIZATION OF SILICON-BASED FILMS BY LASER MODULATED OPTICAL REFLECTANCE AND IR RADIOMETRY

D. Dietzel¹, F. Cerceira², M. Hoffmeyer¹, I. Delgadillo-Holtfort¹, J.L.N. Fotsing¹, J.A. Ferreira², J. Pelzl¹, B.K. Bein¹

¹Exp.Phys. III, Solid State Spectroscopy, Ruhr University, D-44780 Bochum, Germany
²Depart. de Fisica, Universidade do Minho, P-4709 Braga Codex, Portugal

Abstract

Si-based films, deposited by reactive magnetron sputtering on glass and silicon substrates have been analyzed with the help of laser-modulated optical reflectance and IR radiometry. The results are discussed with respect to the thermal and charge carrier transport properties. Semiconductor properties have been identified both for micro-crystalline and amorphous films

1. Introduction

Two photothermal techniques, both using modulated laser beam excitation in the visible spectrum but different detection channels, namely probe beam sensing of the optical reflectance and radiometry in the near and mid infrared, have been applied to analyze CdInSe films and different Si-based films, deposited by sputtering on glass and silicon. While the IR radiometry is mainly sensitive to the thermo-optical transport properties, the modulated optical reflectance can give additional information on the charge carrier transport properties in semiconductors. In chapter 2 the two measurement techniques are briefly presented. In chapter 3 the conditions of film deposition are described. Then the results measured for microcrystalline and amorphous films are compared with reference signals of silicon and glassy carbon and discussed with respect to the effective thermal and electronic transport properties.

2. Principles of photothermal measurements

The two photothermal techniques, used here to analyze sputtered films on silicon and glass, rely on the excitation of thermal waves and charge carrier density waves by an Ar ion laser beam, intensity-modulated with the help of an acousto-optic modulator. For the detection of the response, different detection channels are used: the modulated optical reflectance in the visible spectrum (Fig. 1) and IR radiometry in the near and mid infrared, which is based on the detection of the modulated emitted thermal radiation (Fig. 2).

Apart from the beam expansion and the focussing optics, necessary for localized excitation in thermal scanning microscopy based on modulated optical reflectance (Fig. 1), the excitation is similar for the two techniques. For the detection of the optical reflectance signal, the continuous beam of a He-Ne laser is used to probe the reflectance of the sample’s surface,

\[ S(t) \propto \Delta R = \left[ \frac{\partial R(T,n)}{\partial T} \right] \cdot \Delta T + \left[ \frac{\partial R(T,n)}{\partial n} \right] \cdot \Delta n \]  

which can vary in semiconducting material due to both temperature oscillations and charge carrier density oscillations, excited by modulated laser light with a photon energy exceeding...
the band gap. The charge carrier density waves (2) and the thermal waves (3) are described by two diffusion equations [1,2]:

\[
\frac{\partial n(\tilde{x}, t)}{\partial t} - \alpha_n \nabla \cdot \nabla n(\tilde{x}, t) + n(\tilde{x}, t)/\tau_c = S(\tilde{x}, t)
\]

(2)

\[
\frac{\partial T(\tilde{x}, t)}{\partial t} - \alpha_T \nabla \cdot \nabla T(\tilde{x}, t) = Q(\tilde{x}, t)/C
\]

(3)

In equ.(2) \( \alpha_n \) is the diffusivity of the charge carriers and \( \tau_c \) their recombination time. \( S(\tilde{x}, t) \) is the absorbed modulated photon flux, directly responsible for the excitation of the charge carrier density oscillations. The term \( n(\tilde{x}, t)/\tau_c \) describes the volume charge carrier recombination rate. The charge carrier diffusion equation (2) is independent of the thermal diffusion equation (3) and can be solved separately. In equ.(3) \( \alpha_T \) is the thermal diffusivity and \( C \) the volume heat capacity. The modulated heat sources consist of two terms

\[
Q(\tilde{x}, t) = (h \nu - E_g) S(\tilde{x}, t) + E_g n(\tilde{x}, t)/\tau_c
\]

(4)

which contribute to the coupling of the thermal wave equation. The first term describes the effect of prompt heating related to fast thermalization of the photon energy \( h \nu \) exceeding the band gap \( E_g \). The second one describes the heat release inherent to the recombination of charge carriers, retarded in time and locally displaced by the charge carrier diffusion. In general, the modulated reflectance signal, sensed by the He-Ne probe beam (Fig. 1), depends on the superposition of the thermal wave and the charge carrier density wave. Both can be separated in frequency dependent measurements due to the fact that the charge carrier diffusion, their recombination, and the thermal wave diffusion are governed by different time constants, and that the temperature coefficient \( R_T = \partial R(T, n)/\partial T \) and the charge carrier density coefficient \( R_{cc} = \partial R(T, n)/\partial n \) of the optical reflectance are opposite in sign.

In layered systems consisting of thin semiconducting films, however, the surface recombination can play the dominant role [3], contributing to surface heat sources only slightly retarded in time with respect to the first term of equ. (4). This means the charge carrier diffusion effects on the measured signal may remain relatively low and cannot be distinguished from the thermal waves. In this latter case, the reflectance signal can be approximated by

![Diagram of laser beam-modulated optical reflectance technique.](image)

Fig. 1: Schematic of the laser beam-modulated optical reflectance technique.
\[ S_i(f) \propto \Delta R = \left[ \frac{\partial R(T,n)}{\partial T} \right] \Delta T \]  

(5)

with \( \Delta T \) the thermal wave, which for the example of an opaque two-layer system is given by

\[ \Delta T(x_s=0,f,t) = \frac{\eta_s I_0}{2\epsilon_s \sqrt{2\pi f}} \left[ \frac{1 + R_{pb}\exp(-2\sigma_s d_s)}{1 - R_{pb}\exp(-2\sigma_s d_s)} \right] \cos(2\pi ft - \pi/4) \]  

(6)

Here \( I_0 \) is the intensity of the Ar ion laser pump beam and \( \eta_b = 1 - R_b \) the photothermal efficiency, with \( R_b \) the reflectance at the wavelength of the Ar ion pump beam. \( R_{pb} = (\epsilon_s/\epsilon_b - 1)/(\epsilon_s/\epsilon_b + 1) \) is the thermal reflection coefficient [4] at the transition between the sputter-deposited thin film and the substrate material, with \( \epsilon_s \) and \( \epsilon_b \) the thermal emissivities of the film and the substrate, respectively. The complex quantity \( \alpha = (1+i)/\mu_{th} \) with i the imaginary unit, and \( \mu_{th} \) the thermal diffusion length

\[ \mu_{th} = (\alpha \tau / \pi f)^{1/2} \]  

(7)

contributes to the damping and phase shift of the thermal wave. Here, \( \alpha \) is the thermal diffusivity and \( d_s \) the thickness of the sputter-deposited thin film.

In Figure 2, the schematic of modulated IR radiometry is shown: a photo-conductive HgCdTe detector and IR optics consisting of two BaF\(_2\) lenses and a cut-on filter allow a detection wavelength interval of 1–12 \( \mu \)m and a maximum focussed solid angle of \( \Omega_{\text{sc}} = 0.196 \) steradians. A lock-in amplifier is used to filter the small periodical variations of IR emission

\[ \Delta M(T,f) = \gamma^4(T) (\epsilon_s(T) \sigma_{\text{tot}} T^3) \Delta T(f) \]  

(8)

related to the thermal waves \( \Delta T(f) \) from the comparatively large radiation background

\[ M(T) = \gamma(T) \epsilon_s(T) \sigma_{\text{tot}} T^4 \]  

(9)

at the stationary sample temperature \( T \). By comparing the modulated (8) and the stationary radiometric signals (9), the sample’s emissivity \( \epsilon_s(T) \) can be eliminated and the thermal wave response

\[ \Delta T(f) = \frac{\gamma(T) T M(T,f)}{\gamma^4(T) \Delta M(T,f)} \]  

(10)

is obtained directly, which in the case of a two-layer system is equal to equ.(6). The quantities \( \gamma(T) \) and \( \gamma^4(T) \) are the detection efficiencies for modulated and stationary IR radiation and depend on technical parameters of the IR detection system. Thermal waves of about 44 \( \mu \)K, 15 \( \mu \)K, and 9 \( \mu \)K amplitude have been detected with this system at stationary sample temperatures of 300 K, 400 K and 500 K, respectively [5].

3. Measurements on Si-based thin films on Glass and Silicon

The analyzed Si-based films (b1, b2, d13) have been produced by reactive magnetron sputtering using a chamber Alcatel SCM 650. The target consisted of a hyperpure silicon wafer spaced at about 50 mm from the substrates. The films were deposited in a hydrogen rich atmosphere, applying different RF power: 80 W for sample d13, 200 W for b2, and 400 W for...
b1. Previous work [6] has shown that low RF powers in a hydrogen-rich atmosphere contribute to thin films with silicon microcrystals and that high RF powers contribute to amorphous material. X-ray analysis supplemented by Raman spectroscopy [7] confirmed that the film b1 is amorphous and the other two films show silicon micro-crystals embedded in an amorphous matrix. The film d13 is more crystalline with a crystal volume fraction around 48% and an average crystal size of 65 Å than film b2 with a crystal volume fraction of 45% and an average crystal size between 50 - 60 Å. The film thickness has been determined from the transmission spectra by Swanepoel's method [8]: 0.642 μm for sample d13, 1.051 μm for b2, and 1.061 μm for b1. The composition of the films has been obtained from ERD/RBS: about 56% of silicon, 25% of hydrogen, and 19% of oxygen.

Apart from the sensitivity with respect to semiconductor properties, another special advantage of the reflectance technique is used here: it can be applied to film systems on glass, to measure and control the thermal and semiconductor properties of film deposition from the rear surface across the glass substrate. In Fig. 3 different films deposited by sputtering are qualitatively compared with a Si sample (○), which clearly shows the frequency characteristics of semiconductor material: from 100 Hz to 20 kHz, the measured amplitudes decrease, and above 20 kHz they increase again with frequency. This is due to the fact that the charge carrier contributions in Silicon are dominant at higher frequencies, while the thermal wave contributions decrease in the high frequency limit according to $f^{-1/2}$ (equ. 6). The amplitude of the amorphous Si-based film (b1 *) also shows the typical behavior of charge carrier contributions: From about 1 kHz to 10 kHz it decreases strongly with frequency, and above 10 kHz the decrease with frequency is less pronounced. Since the thermal effects and the charge carrier effects on the modulated reflectance signal (equ. 1) are opposite in sign, the resulting measured signal already strongly decreases at intermediate frequencies, while the decrease is less at higher frequencies where the charge carrier contributions are comparatively larger.

Fig. 3: Photo-modulated optical reflectance amplitudes of Si-based films (b2 , b1 *) and a CIS film on glass (○), compared with the amplitudes found for Si (○).

Fig. 4: Phases of the modulated reflectance signals of two Si-based films (b2 , b1 *) and CIS (○) films on glass, in comparison with the phases measured for Si (○).
At first glance, no definite information on the thermal or charge carrier contributions can be obtained from the frequency-dependence of the amplitudes measured for the microcrystalline Si-based film (b2) and the CIS film (Φ) in Fig. 3. Such information is obtained, however, when the measured phases are also considered. In figure 4, the phases of these two samples (Φ) decrease by a value of about 60° from an initial value of 165° at low frequencies, f = 100 Hz, to about 105° at 20 kHz. This decrease, which is characteristic for thermal wave contributions of semitransparent systems, accelerates considerably above 20 kHz, where a further decay of about 105° is found. This behavior is characteristic for small charge carrier wave contributions, which become only comparable or dominant in comparison to the thermal wave contributions above about 20 kHz. Since the charge carrier coefficient \( R_c = \frac{\partial R(T,n)}{\partial n} \) and the temperature coefficient \( R_T = \frac{\partial R(T,n)}{\partial T} \) of the optical reflectance are opposite in sign, the dominant charge carrier waves contribute to a phase shift of about 180°, a value not achievable by any thermal wave process.

The Si sample, already characterized by the amplitudes with the second relative maximum due to charge carrier contributions above 30 kHz (Fig. 3), also shows the typical strong decrease of the phases (Φ) in Figure 4.

The phases of the Si-based amorphous film (b1 ⋆) deviate from the behavior of the other samples in a very characteristic way: at low frequencies, there is already a strong decrease of the phase which, however, recovers between about 8 – 20 kHz. At still higher frequencies the phase then continues to decay. From this behavior we can conclude that there may be two dominant contributions measured at lower frequencies at the transition between glass substrate and Si-film: (i) Thermal wave diffusior together with charge carrier diffusior and recombination at the interface between glass substrate and Si-film, where the modulated reflectance is probed by the HeNe laser beam and (ii) additional charge carrier recombination at the front surface of the amorphous film. At higher modulation frequencies, \( f > 20 \) kHz, the heat sources related to the charge carrier recombination at the sample’s front surface can no longer contribute to the modulated reflectance signal measured at the transition between glass substrate and film, as the damping of the thermal wave across the amorphous film is too strong due to the reduced thermal diffusivity and the thickness of about 1 μm of the film.

The amplitudes, measured with the help of modulated IR radiometry for the micro-crystalline Si-based film b2 or glass ( ) and on Silicon ( ) are shown in Figure 5, in comparison with reference
signals measured for glassy carbon (X) and Si (O). All signals are far from the noise limit and thus can be interpreted quantitatively. The amplitudes measured for Si and the micro-crystalline film or Si are close to each other at low frequencies, whereas the signals of the sample with the film is higher by a factor of 3-4 at intermediate frequencies, which means according to eqn. (6) that the effusivity of the micro-crystalline film is considerably below the effusivity of Si. Such a behavior cannot be seen for the film deposited on glass under the same conditions. This is due to the fact, that the effusivity of the quartz glass substrate is below the effusivity of the Si-based micro-crystalline film and much below that of the Si substrate.

For a more detailed quantitative interpretation the IR signals measured for the films are calibrated

\[ s_n^{-1} (f^{-1/2}) = \frac{\Delta M_{\text{film}} (f)}{\Delta M_{\text{car}} (f)} \]  

with the help of reference signals of homogeneous opaque glassy carbon of known thermo-optical properties. For the quantitative interpretation, the resulting inverse normalized signals have then to be approximated by solutions based on the two-layer model of finite thickness, which is semi-transparent both in the visible and infrared spectrum [9].

References