Passivation properties of nitric/phosphoric etching on CdTe films: Influence of the etching time and nitric acid concentration

O. Vigil-Galán [a], A Cruz-Orea [b], C. Mejía-García [a], J. Fandiño [c],[*], M.F. García-Sánchez [d]

[a] Escuela Superior de Física y Matemáticas (ESFM), Instituto Politécnico Nacional (IPN), C. P. 07738, México D. F., México
[b] Departamento de Física, CINVESTAV-IPN, AP.14-740, CP 07360, México DF, México
[c] Universidad Autónoma de la Ciudad de México, Av. la Corona 320, Col. Loma la Palma, Gustavo A. Madero, 07160, México D.F., México
[d] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán 04510, México D.F., México

ARTICLE INFO

ABSTRACT

The chemical etch of CdTe surfaces with a mixture of phosphoric and nitric acids is used in research labs in order to enhance the back-contact formation in CdS/CdTe solar cells. However, the possible passivation effect of this approach has not been studied. In this work we report an investigation about the etching effect of nitric/phosphoric acid mixtures with different etching times (0, 30, 40 and 50 s) and variable concentrations of the nitric acid upon the surface recombination velocity of CdTe films deposited by close space vapor transport. Surface recombination velocities with values as low as 93 cm/s were achieved.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, great efforts have been made toward the improvement in the cell open-circuit voltage and fill factor on CdS/CdTe-based devices. A known approach to achieve these goals consists on reducing the back surface recombination velocity by means of surface treatments [1,2]. Wet chemical etching of CdTe is generally accepted to create a Te-rich region on the CdTe surface, improving back-contact formation. Usually, contact pre-deposition etching treatments are made on CdTe by using either a dilute solution of bromine in methanol (Br$_2$-MeOH) or a mixture of nitric and phosphoric acids in water, known as NP etching. These etchings allow CdTe surface smoothening, cleaning it from oxides and other contaminations. At the same time, wet chemical etch creates a Te-rich surface layer on CdTe which effectively results in a p$^+$-doped zone that produces a back surface field. It has been demonstrated that NP etching is more effective than that using Br$_2$-MeOH, considering the formation of the Te-rich region on CdTe [3]. However, the study of surface passivation achieved by means of a chemical etching has not been reported on CdTe. It is well known that the surface recombination velocity (SRV) has a significant influence on the device's performance [4]. Particularly, low values of SRV are required at the back contact of CdTe-based solar cells in order to prevent degradation in quantum efficiency, electrical properties and therefore in the final conversion efficiency of the device.

Photoacoustic (PA) measurements allow quantitative SRV determination in semiconductor samples [5–7]. The PA technique is based on the generation of heat inside the sample as a consequence of the absorption of periodically modulated light, and the subsequent non-radiative recombination processes, which are connected (among other physical parameters) to the SRV. The contribution from non-radiative recombination at the surface of the material to the total recombination is reduced as a consequence of the surface passivation process. Another indirect measurement of the SRV can be obtained by photoluminescence (PL), which is related to the radiative recombination from the sample. It has been well established that the PL technique is a straightforward method which accounts qualitatively for SRV, since the PL signal depends directly on the photogenerated minority carrier distribution near the surface [8,9].

In this work, the influence of different NP chemical etching conditions on the CSVT-CdTe samples grown by closed space vapour transport (CSVT) are analysed using PA and PL and the results are discussed.

2. Materials and methods

CdTe thin films were deposited on 3 mm thick commercial conducting glass (SnO$_2$:F) substrates by the CSVT-HW (Hot Wall) method, using CdTe powders (6N purity). Further details of this deposition technique have been presented in [10]. The substrate and source temperatures were 550 and 650 °C, respectively. The deposition time was adjusted in order to obtain samples with similar thickness of about 4 μm. For thermal treatment, a 200 nm CdCl$_2$ layer

* Corresponding author. Tel.: +52 55 36912050x18288; fax: +52 55 53233787.
E-mail address: jfand72@yahoo.com (J. Fandiño).

was deposited by CSVT over the CdTe films and then annealed at 450 °C during 30 min in Ar atmosphere.

Two NP solutions with identical concentration of phosphoric acid (10.70 mol/L) were used through this study; the main difference between them was the concentration of nitric acid which was 0.13 mol/L for solution A and 0.17 mol/L for solution B. The CdTe surfaces were etched with solution A at three different times: 30, 40 and 50 s while solution B was used for an etching time of 30 s, in order to compare with solution A. The samples were named A-30, A-40, A-50 and B-30, respectively.

The experimental set-up used for the PA measurements corresponds to the open photoacoustic cell (OPC) configuration [11,12]. In this configuration the sample is attached on the front sound inlet of an electret microphone and its surface is irradiated by an intensity modulated laser beam which is absorbed by the sample and converted into heat due to the non-radiative de-excitation processes. For this configuration, the 514 nm line of a 50 mW Ar-ion laser was used as the light source and its intensity was modulated using a mechanical optical chopper. Samples were fixed with vacuum grease on the top of the electret microphone. The PA signal from the microphone was amplified with the aid of a lock-in amplifier and recorded as a function of the light modulation frequency, f.

For the PL measurements we used an Ar^+ laser tuned at 4880 Å, (2.54 eV), focused on the sample through a cylindrical lens in order to avoid overheating. The outgoing radiation was focused on the entrance slit of a double monochromator. The detection was carried out by means of a thermoelectrically cooled photomultiplier tube coupled to a photon counter. The sample was attached to the cold finger of a He closed-cycle refrigeration system in order to reach low temperatures (10 K). All PL spectra were corrected for the spectral response of the system.

Chemical analysis at the samples surface was performed in a scanning electron microscopy by energy dispersive X-ray (EDX) micro-analysis system (XL 30 FEG/SIRION with focused ion- and electron-beam, energy dispersive X-ray spectroscopy, and energy dispersive angle x-ray GENESIS 4000).

3. Theory

In order to obtain the theoretical PA signal in semiconductor samples, the heat diffusion equation together with the continuity equation have been solved for free carriers in semiconductors. Both equations take into account the heat sources resulting from the light absorption in semiconductors. If the photon energy of the incident laser beam is greater than the semiconductor band gap energy it is possible to identify basically three heat sources: the intraband non-radiative thermalization, the non-radiative electron-hole pair recombination in the bulk and the recombination at the sample surface. It has been found that, for optically opaque semiconductors, the pressure fluctuation in the PA cell for the OPC detection configuration is given by [5,13]:

$$\delta P = \frac{2\varepsilon I_0 P_0}{T_0 l_g \sigma_g k_s \sigma_s} \left\{ \left[\frac{\varepsilon-1}{\varepsilon}\right] e^{-l_s \sigma_s} + \frac{F\sigma_s}{D\gamma\tau} \left[\frac{1}{\sigma^2-\gamma^2} + \frac{v\tau}{\sigma_s}\right] \right\} \quad (1)$$

where ϵ is the ratio between the semiconductor band gap energy E_g, and the incident light photon energy of intensity I_0. P_0 (T_0) is the ambient pressure (temperature). The parameters l_i ($i=g, s$) are the thickness of the PA cell gas chamber (g), and the sample (s). The complex thermal diffusion coefficient $\sigma_i = (1+j)a_i$ is given in terms of $a_i = \sqrt{\pi f / \alpha_i}$, where α_i (κ_i) are the respective thermal diffusivities (conductivities), $j=\sqrt{-1}$; D is the carrier diffusion coefficient, τ the non-radiative carrier recombination time, $\gamma = (1/D\tau)^{1/2}(1+j\omega\tau)^{1/2}$, with $\omega=2\pi f$, and f the light modulation frequency. The parameter F

depends on γ and also on the surface recombination velocity (v_0) and the recombination velocity at the glass interface v, explicitly:

$$F = \left[(1 + r_0)(1 + r)e^{\gamma l s} - (1-r)(1-r_0)e^{-\gamma l s}\right]^{-1} \quad (2)$$

where $r = v/D\gamma$ and $r_0 = v_0/D\gamma$.

The first term in Eq. (1), scaling exponentially with the modulation frequency as, $(1/f) \, exp\left(l_s\sqrt{\pi f / \alpha_s}\right)$ is the thermal diffusion contribution from an instantaneous heat source, as described by the RG model [14]. The second term in the large square brackets of Eq. (1), which scales as $f^{-1.5}$, is the contribution of the nonradiative bulk recombination. Finally, the last term in Eq. (1) varying as $f^{-1.0}$ is the contribution from the nonradiative surface recombination.

4. Results and discussion

Both the amplitude and phase of the PA signal were measured as functions of the modulated frequency in the range between 80 and 200 Hz. Fig. 1 shows the behavior of the experimental PA signal phase data (solid circles) on A-30 sample. Eq. (1) was fitted, using GNUPLOT version 4.2, to the experimental PA phase data in order to obtain the surface recombination velocity v_0 as a fitting parameter. The fixed parameters used in this fitting were $\alpha_s = 3 \times 10^{-3}$ cm^2/s and $\alpha_g = 0.21$ cm^2/s corresponding to the thermal diffusivities of glass [15] and air respectively, l_s is the measured sample thickness, and the carrier diffusion coefficient was taken as D = 3.8 cm^2/s [15]. The best τ value to fit Eq. (1) to the experimental data was $\tau = 0.1$ ms for the studied samples. This τ value is in the same order of that reported by Bernal-Alvarado et al., $\tau = 0.35$ ms, for a polycrystal CdTe/glass system studied also by OPC technique [16]. The parameter τ is an effective time that takes into account non-radiative recombination times. Also we neglected the recombination velocity at the CdTe-glass interface. The solid line in Fig. 1 shows the best fit of Eq. (1) to the experimental data. Similar signal phase fittings were obtained for the other samples. The values of surface recombination velocity obtained in each case are reported in Table 1.

The etching time equal to zero corresponds to the sample without etching treatment in order to compare v_0 with the treated samples. It is possible to see that the minimum of surface recombination velocity for "A" samples is reached at 30 s of chemical etch. The results also show that the etching with B-30 produces the highest passivation effect. The obtained v_0 value in this sample (93 cm/s) is lower than those reported for CdTe polycrystalline films deposited on glass slides by hot-wall closed-space vapor transport [15,16] and CdTe mono-crystal [13].
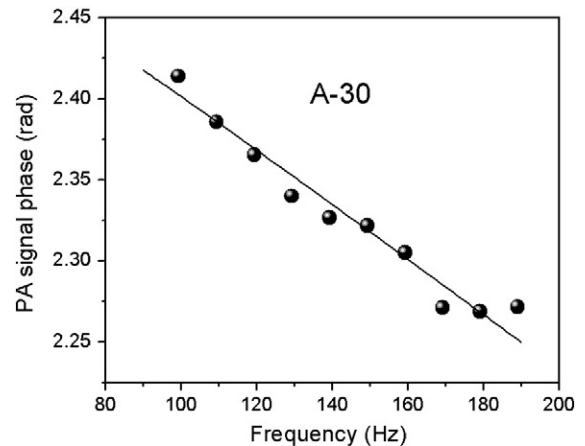

Fig. 1. PA signal phase vs. light modulation frequency for sample with 30 s of etching time in solution A. The solid symbols are the experimental data and the solid line is the best fitting of Eq. (1) to the experimental data.

Table 1
Chemical composition and SRV values from EDX and PA measurements, respectively. The result for the non-etched sample is shown for comparison.

Sample	Conc. Cd (at.%)	Conc. Te (at.%)	Cd/Te	Etching time (s)	SRV (cm/s)
Non etched	49.5	50.5	0.98	0	311
A-30	35.2	64.8	0.54	30	207
A-40	33.8	66.2	0.51	40	212
A-50	32.1	67.9	0.47	50	247
B-30	30.7	69.3	0.44	30	93

The enhancement in the PL intensity was also used to evaluate the efficiency of the passivation at the surface. The PL spectra of samples without etching and etched with the solution A are depicted in Fig. 2a. The non-etched sample spectrum is characterized for the emission line at 1.589 eV of exciton bounded on acceptor (A^o-X), a wide band around 1.44 eV region with few phonon replicas separated approximately by 22 meV and the signal emission at 1.55 eV, which in fact consist of two peaks separated by around 6–8 meV [17], has been related to Cd vacancies and Te precipitate at the surface of CdTe. It is observed that the intensity of the A^o-X line decreases and the bands related with the Cd vacancies increase as the etching time rises. PL spectra of sample etched with solution B is shown in Fig. 2b. A relative increase in the peak intensity associate to Te precipitate is observed. These results are in correspondence with results of EDX measurements (Table 1), where the maximum concentration at 69.3% of Te was measured in the B-30 sample. This behavior could be associated to the passivation effect of Te at the CdTe surface. It can be noticed in Table 1 that the Cd/Te ratio shows a decreasing tendency with the
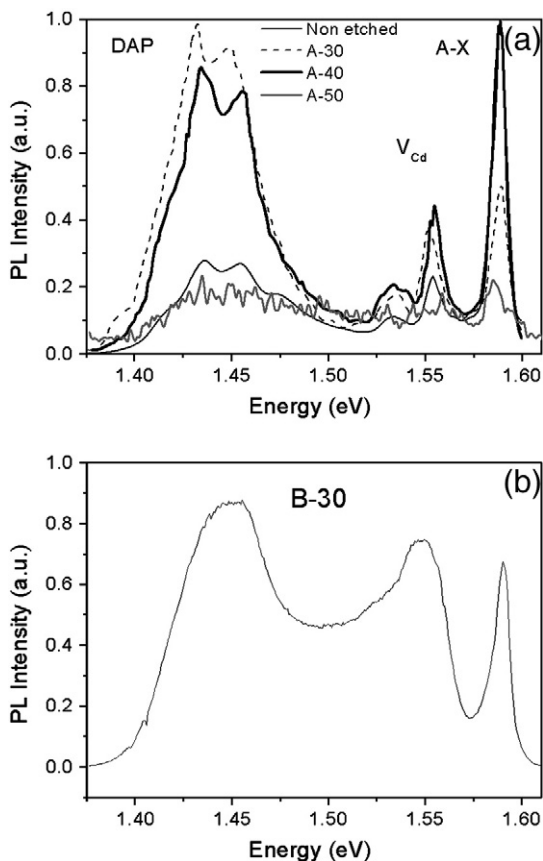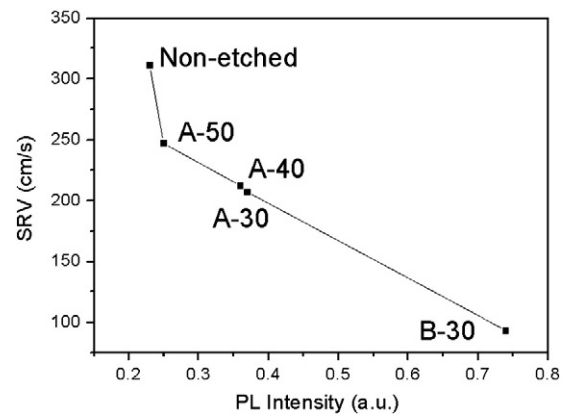

Fig. 3. Correlation between SRV (from PA measurements) and I_{VCd} peak intensity (from PL measurements) for different NP etching conditions. Solid curve is a simple guide to the eye.

increase of the etching time for the A solutions or with the increase of the nitric acid concentration. These results confirm the selective removal of Cd atoms by the chemical etch to produce a Te rich (p+) region near the CdTe surface. In a first stage the NP solution removes Cd atoms, contributing to surface passivation, but the ulterior increase of etching time damages the surface and the layers beneath it in a way that affect the SRV.

The relation of SRV with the PL peak intensity associated with the cadmium vacancies (I_{VCd}) is shown in Fig. 3. Higher values in the I_{VCd} peak intensity (with increase in the formation of elemental Te) corresponds to lower SRV values, meaning an increment in the CdTe surface passivation.

From the above results the NP etching on the CSVT-CdTe samples produces an effective surface passivation of the CdTe surface due to the formation of elemental Te rich region. Aspects related with possible degradation effect in the physical bulk properties of the absorber CdTe films, etched with B-30 are in progress.

5. Conclusions

The passivation properties of NP etching on p-type polycrystalline CdTe layers, deposited by CSVT method have been demonstrated. The etching reduce surface recombination velocity, calculated from photoacoustic measurements, but the increase of etching time for more than 30 s increases again the SRV. A minimum value of 93 cm/s for the SRV was achieved when the concentration of nitric acid was increased to 0.17 mol/L. Photoacoustic measurements shown that passivation in directly related to the vacancies of Cd produces by the etch of samples.

Fig. 2. (a) PL spectra (10 K) of etched CdTe layers of the samples of group A etching at 20, 30 and 40 s. The non-etched sample is shown for comparison. (b) PL spectra (10 K) of CdTe sample etched with solution B-30.

References

[1] P.V. Meyers, Solar Cells 27 (1989) 91.
[2] W. Diehl, V. Sittinger, B. Szyszka, Surf. Coat. Technol. 193 (2005) 329.
[3] D.L. Bätzner, R. Wendt, A. Romeo, H. Zogg, A.N. Tiwari, Thin Solid Films 361–362 (2000) 463.
[4] K.J. Hsiao, J.R. Sites, Proc. 34st IEEE Photovoltaic Specialists Conf., Philadelphia, U.S.A., Jun 7-12 2009, p. 001846.
[5] A. Pinto Neto, H. Vargas, N.F. Leite, L.C.M. Miranda, Phys. Rev. B 40 (1989) 3924.
[6] I. Riech, G. Santana, P. Díaz, A. Morales-Acevedo, H. Vargas, E. Marín, Semicond. Sci. Technol. 14 (1999) 543.
[7] I. Reich, P. Díaz, T. Prutskij, J. Mendoza, H. Vargas, E. Marín, J. Appl. Phys. 86 (1999) 6222.
[8] O. Vigil-Galán, J.N. Ximello-Quiebras, J. Aguilar-Hérnandez, G. Contreras-Puente, A. Cruz Orea, J.G. Mendoza-Álvarez, J.A. Cardona-Bedoya, C.M. Ruiz, V. Bermúdez, Semicond. Sci. Technol. 21 (2006) 76.
[9] O. Vigil Galán, J. Vidal Larramendi, I. Riech, G. Peña Rodríguez, A. Iribarren, J. Aguilar-Hérnandez, G. Contreras-Puente, Semicond. Sci. Technol. 17 (2002) 1193.
[10] G. Contreras-Puente, O. Vigil-Galán, J. Vidal-Larramendi, F. Cruz-Gandarilla, M. Hesiquio-Garduño, J. Aguilar-Hernández, A. Cruz-Orea, Thin Solid Films 387 (2001) 50.

[11] I. Delgadillo, A. Cruz-Orea, H. Vargas, J.J. Alvarado-Gil, M. Vargas, High Temp. High Pressures 30 (1998) 613.
[12] A. Cruz-Orea, I. Delgadillo, H. Vargas, J.L. Pichardo, J.J. Alvarado-Gil, L.C.M. Miranda, Solid State Comm. 100 (1996) 855.
[13] I. Delgadillo, M. Vargas, A. Cruz-Orea, J.J. Alvarado-Gil, R. Baquero, F. Sánchez-Sinencio, H. Vargas, Appl. Phys. B 64 (1997) 97.
[14] A. Rosencwaig, A. Gersho, J. Appl. Phys. 47 (1976) 64.
[15] M.A. González-T, A. Cruz-Orea, M. de L. Albor-A, F. de L. Castillo-A, Thin Solid Films 480–481 (2005) 358.
[16] J. Bernal-Alvarado, M. Vargas, J.J. Alvarado-Gil, I. Delgadillo, A. Cruz-Orea, H. Vargas, M. Tufiño-Velázquez, M.L. Albor-Aguilera, M.A. González-Trujillo, J. Appl. Phys. 83 (1998) 3807.
[17] J. Aguilar-Hernández, M. Cárdenas-García, G. Contreras-Puente, J. Vidal-Larramendi, Mater. Sci. Eng., B 102 (2003) 203.