JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 1, January 2007, p. 209 - 212

Potential gas sensor applications of semiconductor thin films based on changes in photoresponse

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A method for improving the discrimination of semiconductor thin-film gas sensors, which utilises the amplitude and phase of the photocurrent response to a modulated light source, is proposed. The photoconductivity of microcrystalline silicon films is examined before and after exposure to the vapour of an iodine solution in ethanol. Preliminary results are presented which suggest that the density and/or capture properties of localised states may be reversibly modified. For cadmium selenide however, a small but systematic temperature-dependent phase *lead* is observed in this material at low frequencies, even under vacuum-annealed conditions. This is in contrast to present theory, which predicts that for an arbitrary localised state distribution the photocurrent response must *lag* the applied excitation.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: Gas sensors, Modulated photoconductivity, Semiconductors, Thin films

1. Introduction

The electronic properties of semiconductor thin films are sensitive to adsorption of gas molecules, and thus may be utilised in gas sensors [1]. Adsorption may change the carrier concentration by doping, by altering the concentration of electronic defects or, in the case of polar molecules, by surface band-bending. The mobility may also be affected if there is a change in the conduction process, for example an alteration of the potential barrier height between crystalline grains. Such effects may be manifested in changes in the dark- and photo-conductivity [2] and photoluminescence.

The conductivity may be increased or decreased by these effects, which penetrate to varying degrees into the film, and may thus influence both the surface and bulk properties. The film morphology, tied to composition and deposition conditions, also plays a significant role.

By selecting appropriate films, the sensitivity to specific gases may be enhanced, which enables discrimination between adsorbed species. Frequently however, different gases produce similar changes in conductivity, and further measurements, e.g. of the response time or activation energy, are required to distinguish between them.

In this paper, we propose a method for discriminating between species adsorbed on a *single* film, based on measurement of the amplitude and phase of the photocurrent response to a modulated light source. This amounts to applying the modulated photoconductivity (MPC) technique [3], used in the study of the energy distribution and capture properties of the localised density of states (DOS) in disordered thin films.

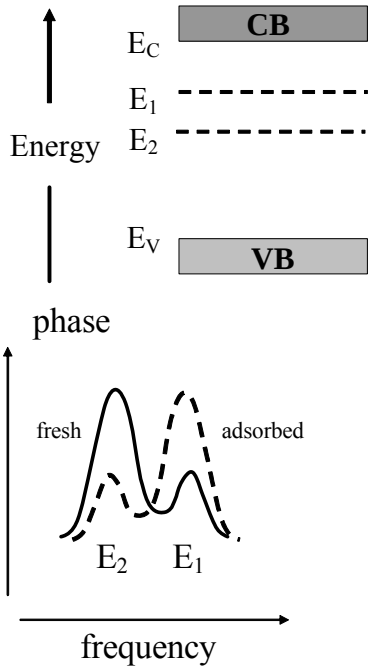

Fig. 1. Changes in the density of localised states at E_1 and E_2, brought about by adsorption of molecules at specific sites, affects the phase of the photocurrent.

Fig. 1 illustrates schematically a possible linkage between the density of gap states and the MPC signal. The basis of the proposed gas sensing application is that one or more of the properties of defect states, e.g. density, capture coefficient, energy position or width of the distribution, is specifically affected by adsorbed species. This interaction is perhaps most likely to occur at surface defects, thus

porous or permeable very thin films, with a high surface-to-volume ratio, may be favoured in this application.

There are two variants of MPC spectroscopy:

***High frequency (HF) regime*:**

At higher modulation frequencies and low carrier generation rates, the response is determined mainly by emission of carriers from states above the quasi-Fermi level. By varying the angular frequency ω and recording the photocurrent amplitude $|I(\omega)|$ and phase $\varphi(\omega)$ the DOS distribution (referred to as HFDOS) may be probed [3] :

$$N_{HF}(E_\omega) = \frac{2G_\omega qFA}{(C_n/\mu)\pi kT} \times \frac{\sin(\varphi(\omega))}{|I(\omega)|}, \qquad E_\omega = E_C - kT\ln(\nu_0/\omega) \tag{1}$$

G_ω is the ac carrier generation rate per unit volume, q the elementary charge, F the electric field, A the conduction cross-section, ν_0 the attempt-to-escape frequency (here assumed to be 10^{12} s^{-1}), k is Boltzmann's constant, E_C the conduction band reference energy and T the absolute temperature. The HFDOS contains a factor (C_n/μ) where C_n is the capture coefficient and μ the free carrier mobility.

Low frequency (LF) regime:

At higher generation rates, when the photocarrier density is much greater than the thermal carrier density, the phase response becomes linear at sufficiently low frequencies. Under these conditions, carrier capture and subsequent recombination in states at E_t , close to the quasi-Fermi level E_{Fn} , controls the ac response, and the LFDOS is given by [3]:

$$N_{LF}(E_t) = \frac{2G_{dc}}{kT} \times \frac{\tan(\varphi)}{\omega}, \quad E_t \approx E_{Fn} \tag{2}$$

G_{dc} is the steady photocarrier generation rate per unit volume. This expression contains only experimentally measurable quantities and in principle enables the DOS distribution to be probed by varying $\Delta E_{Fn} = kT\ln(I_{dc}/I_0)$, where I_{dc} and I_0 are respectively the steady-state photocurrent and the dark current, through appropriate adjustments of G_{dc} and T.

2. Experimental

Fig. 2 illustrates the experimental set-up used to measure the modulated photocurrent. In this development work, the sample was mounted in a vacuum cryostat into which gases could be introduced and then pumped out. The films studied were PECVD microcrystalline silicon (μc-Si:H) [4] and thermally-evaporated cadmium selenide (CdSe) [5]. Details of the deposition procedures are given in these references. Annealing consisted of heating at typically 90 °C under vacuum for up to 1 hour. Exposure to vapours was from a soaked tissue placed in the chamber.

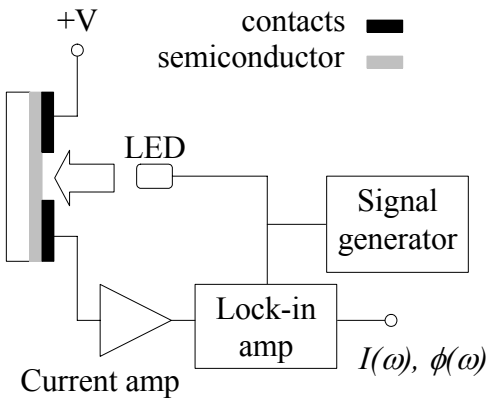

Fig. 2. MPC/Sensor experimental set-up.

Recent work [6] has shown that these films show a significant sensitivity to polar molecules such as water and ammonia, and also to the vapour produced by a 1% solution of iodine in ethanol. This solution was shown to be an effective surface defect passivation when applied directly to silicon wafers or epitaxially-grown silicon thin films [7].

3. Results and discussion

3.1. Microcrystalline silicon

The amplitude and phase spectra for a 260 nm thick μc-Si:H in an annealed state, and then after 30 min. exposure to iodine solution vapour are shown in Figs. 3(a) and 3(b). From Raman data, it was determined that the crystalline volume fraction was about 0.6. Data for a single temperature of 300 K are shown here. A flux of $6x10^{11}$ s^{-1} cm^{-2} was applied from a blue LED (430 nm), and the steady state component of the photocurrent is of a similar size to the dc dark current. Except at the lowest frequencies, the data shown fall within the HFDOS regime.

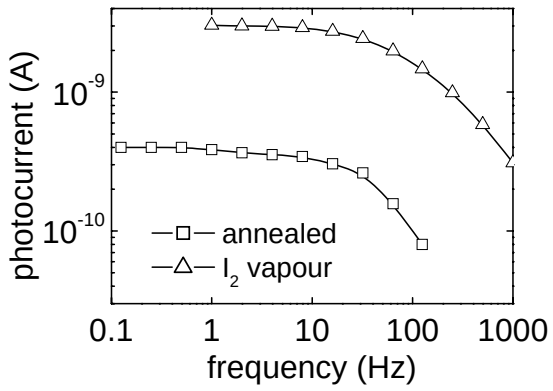

Fig. 3(a). μc-Si:H amplitude spectrum.

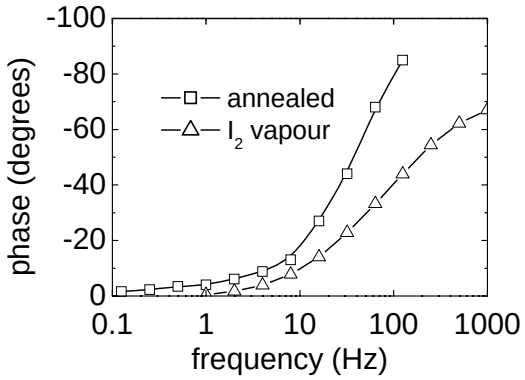

Fig. 3(b). μc-Si:H phase spectrum.

It can be seen from Fig 3(a) that vapour adsorption increases the photoconductivity by about one order of magnitude. The HFDOS shown in Fig. 4, calculated using equation 1, indicates a general reduction in the effect of deep states, and also some small changes in detail. However, as the activation energy of this sample was approximately 0.55 eV, the downturn in the apparent DOS of the exposed sample at about 0.6 eV may reflect a change in the occupancy, rather than the density, of deep states.

The LFDOS may be calculated from the data in Fig. 3(b) using equation 2, from $tan(\phi)/\omega$ at the lowest frequencies. Since the absorption depth for blue light is about 100 nm, $G_{DC} = 6x10^{16}$ cm^{-3} s^{-1}.

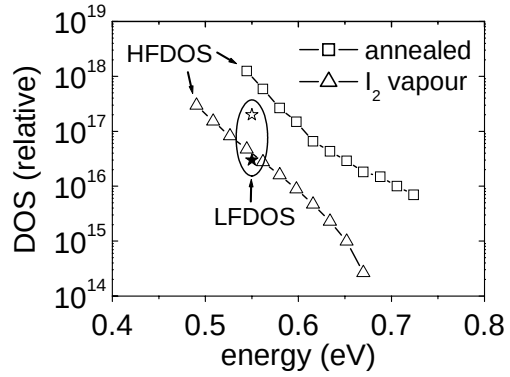

Fig. 4. μc-Si:H DOS distributions.

In the annealed state, a DOS of $2x10^{17}$ cm^{-3} eV^{-1} is obtained, falling to $3x10^{16}$ cm^{-3} eV^{-1} after exposure to iodine solution vapour. By comparing the dark- and photo-conductivity, the quasi-Fermi level in this case is located close to the equilibrium value. Thus, both the HF and LF DOS values indicate a significant reduction in the deep defect density following exposure to iodine.

Although the reversibility of this process has not been rigorously examined using MPC, several annealing/exposure cycles have been carried out and the steady-state photocurrent and dark current values are reproducible.

3.2. Cadmium selenide

We recently reported [6] a study that sought to identify deposition conditions for micro- and nanocrystalline CdSe (and also CdS) films giving optimal electronic sensitivity to gas adsorption. This study was based on steady-state and dark conductivity measurements. It was concluded that for CdSe, the best films were obtained by step-by-step deposition, giving an enhanced interfacial contact area. Although the MPC measurements on these samples are not yet completed, we report here some earlier results on CdSe single layers, which enable us to assess the general suitability of the MPC method as a defect spectroscopy.

Fig. 5 shows the MPC phase response for a one-step deposited CdSe film, having a thickness of 100 nm and grain size of ~260 x 130 nm, over the temperature range 100 to 320 K. At frequencies above 100 Hz, we find a steadily increasing phase lag, typical of most disordered semiconductors. However, at lower frequencies, the phase shift becomes *positive* (a phase *lead*), and reaches a peak before approaching zero as the frequency is further reduced. It should be borne in mind that the phase shifts are quite small, a few degrees, and features such as this are at the limit of system resolution. However the curves shift systematically with temperature, and samples of amorphous silicon measured using similar instrument settings do not show this behaviour. The amplitude spectra also show a corresponding small increase with increasing frequency.

At present, the cause of this is unknown although it is possibly related to the higher crystallinity of CdSe samples. Similar phase leads, in highly crystalline μc-Si:H, and phase shifts which do not extrapolate to zero at zero frequency, have also been observed by others [8].

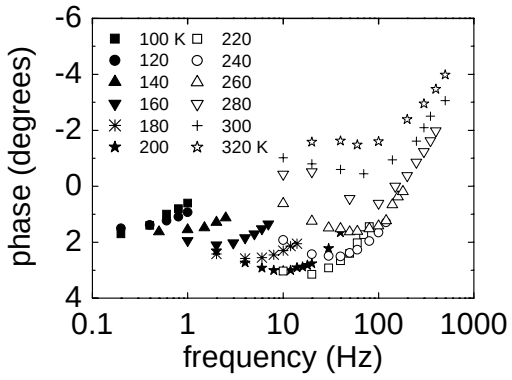

Fig. 5. Phase spectrum for a CdSe sample.

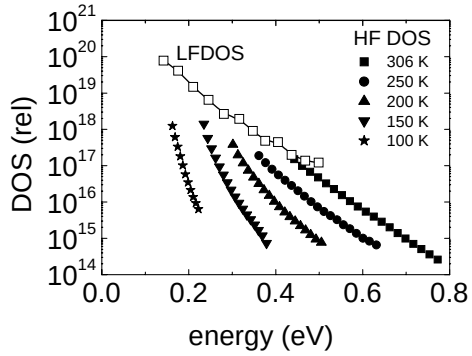

Fig. 6. HF and LF DOS for CdSe.

Fig. 6 shows HFDOS and LFDOS plots for the CdSe film over a range of temperatures. In the case of the LFDOS, reducing the temperature moves the quasi-Fermi level to shallower energies, and in the HFDOS the states involved in emission at a given rate are also shallower, enabling a wider energy range to be probed. The LFDOS here is calculated from the slope of the straight line section of the phase plots, essentially ignoring the phase lead effect. The HF DOS is unsatisfactory, as there is little if any overlap between sections of the DOS obtained at different temperatures, as is required. The results tentatively suggest a rather featureless exponential distribution of the characteristic energy - 48 meV, in contrast to earlier thermally-stimulated current and transient photocurrent work [9] where structure in the DOS was reported.

4. Conclusions

Modulated photoconductivity (MPC) measurements on microcrystalline silicon films firstly annealed and then exposed to the vapour of iodine in ethanol indicate that the density of deep states is reduced. This may be associated with a passivation of defects, but possibly also with a Fermi level shift due to band bending, which fills the deep states. The possibility to discriminate one species of adsorbate from another using MPC has not yet been confirmed. MPC on CdSe films even in the annealed state yields a phase *lead* at low frequencies, in contrast to the phase lag reported for most other disordered materials. We believe this is not an experimental artifact, though it is presently not understood. Future work will address more closely the issue of discrimination, and the possibility of sensor enhancement through the use of functionalized materials.

Acknowledgements

This work was supported jointly by NATO Collaborative Linkage Grant PST.CLG.980656 and the Bulgarian Ministry of Education and Science under grant F-1306. We thank technical staff at IPV, Forschungszentrum Jülich for the preparation of silicon samples.

References

[1] G. Sberveglieri (ed.), Gas Sensors, Kluwer, Dordrecht (1992).
[2] B. K. Miremadi, K. Colbow, Y. Harima, Rev. Sci. Instrum. **68**, 3898 (1997).
[3] For a recent review see: J.P. Kleider, C. Longeaud M.E. Gueunier J. Non-Cryst. Sol. **338-340**, 390 (2004).
[4] O. Vetterl, F. Finger, R. Carius, P. Hapke, L. Houben, O. Kluth, A. Lambertz, A. Mück, B. Rech, H. Wagner, Solar Energy Mater. Solar Cells **62**, 97 (2000).
[5] D. Nesheva, D. Arsova, R. Ionov, J. Mater. Sci. **28**, 2183 (1993).
[6] D. Nesheva, Z. Aneva, S.Reynolds, C. Main, A.G. Fitzgerald, to appear in J. Optoelectron. Adv. Mater. (2007).
[7] A. W. Stephens, M. A. Green, Solar Energy Materials and Solar Cells **45**, 255 (1997).
[8] R. Brüggemann, N. Souffi, private communication.
[9] D. Nesheva, S. Reynolds, Z. Aneva, C. Main, Z. Levi, J. Optoelectron. Adv. Mater. **7,** 517 (2005).

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