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ELECTRICAL PROPERTIES OF PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITED GERMANIUM SELENIDE FILMS

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A study of electrical properties of PECVD a-Ge-Se films has been conducted. Steady-state conductivity measurements show that PECVD samples are different from thermally evaporated (TE) layers. The conductivity in the former is thermally activated with much lower activation energy $E\sigma$, never above 0.7 eV. Moreover, the data do not fit with Meyer-Neldel relation which is universally observed in amorphous semiconductors. PECVD of Ge-Se films may provide a way of changing their electrical properties, while essentially preserving the optical ones with respect to TE films. The presence of hydrogen could be responsible for these changes.

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1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) has become one of the standard methods of preparing amorphous silicon-type materials due to the presence of hydrogen which effectively reduces the density of localized gap states [1]. However, PECVD has had considerably less impact on the preparation of chalcogenide layers. After some initial investigations by Fritzsche and co-workers [2,3] failed to show significant differences between PECVD and thermally evaporated (TE) films for the As-S and As-Se systems, interest only picked up again [4, 5, 6], when also a-Ge-Se layers were being produced. In these references the optical properties, infrared (IR) and Raman spectra of these materials were studied.

In this work, we report on steady-state conductivity measurements to study the electronic properties of PECVD Ge-Se films. The results will be compared with those of films prepared through traditional TE technique [7].

2. Samples

Amorphous Ge_xSe_{1-x} films were prepared by 13.5 MHz plasma discharge of hydrogen-diluted mixtures of GeH_4 and H_2Se gasses. All samples examined in this study are listed in Table 1. The molecular fraction of GeH_4 to H_2Se in the gas flow was 1/8, 1/12, 1/18 and 1/24. Electron microprobe analysis showed that the Ge content varies between 40 and 24.5 and the stoichiometric composition $GeSe_2$ is achievable by using a 1/8 ratio [7]. Corning 7059 glass substrates were placed on either the radio frequency (rf) or the grounded (gr) electrode of the reactor; comparable Ge contents were achieved in films on both electrodes. The substrate temperature during deposition was kept at either room temperature or 175 °C. Deposition at high substrate temperature is found to increase the germanium content in the deposited films while the gas ratio is kept constant; 1/12 gas

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ratio for example usually yields 27 at.% germanium, but this amount grows to 35.6 at.% by heating the substrate. Film thickness varies between 0.6 and 2.5 µm. For the conductivity measurements, co-planar gold electrodes were evaporated onto the a-Ge_xSe_{100-x} layers to provide gap cells with an active area of 0.5×10 mm^2.

Extensive sets of measurements were carried out for the dark and photo-conductivity as a function of temperature and - for the photocurrent - light intensity.

3. Dark conductivity

Dark conductivity measurements were made by applying 10 to 100 V across the gap. Selected representative electrical dark conductivity results are shown in Fig. 1. It is clear that for all samples the dark conductivity is thermally activated according to $\sigma = \sigma_0 \exp(-E_\sigma/kT)$ in the temperature range 294 to 400 K. From the curves the activation energy, E_σ, and the prefactor σ_0 were calculated, and the conductivity at room temperature, σ_{300}, was measured for each sample. The parameters E_σ, σ_{300}, and σ_0, are listed in Table 1.

Table 5.1. Deposition and characterisation parameters of PECVD films, showing the gas flow ratio, the electrode involved, substrate temperature, Ge content, room temperature conductivity σ_{300}, conductivity prefactor σ_0, and the activation energies E_σ and E_{ph} of dark and photocurrent.

Sample No.	GeH_4/H_2Se ratio	Electrode type	Substrate temp.(°C)	Ge at. %	σ_{300} $(\Omega.cm)^{-1}$	σ_0 $(\Omega.cm)^{-1}$	E_σ (eV)	E_{ph} (eV)
333	1/8	gr	RT	28.1	5×10^{-14}	8.4×10^{-4}	0.61	0.28
335	1/8	rf	RT	—	9×10^{-14}	1.0×10^{-4}	0.54	0.32
339	1/8	gr	RT	31.9	2×10^{-9}	1.0×10^{-2}	0.40	0.11
340	1/8	rf	RT	33			0.62	- PC
346	1/8	gr	RT	37	2×10^{-13}	1.1×10^{-2}	0.64	0.25
347	1/8	gr	175	40	2×10^{-7}	9.9×10^{-3}	0.28	0.28
348	1/8	rf	175	—	2×10^{-10}	3.4	0.61	0.26
356	1/8	rf	RT	29.7	2×10^{-6}	3.1×10^{-2}	0.25	0.25
357	1/8	gr	RT	30.5	3×10^{-8}	2.2×10^{-3}	0.29	0.27
361	1/12	gr	RT	27.8	3×10^{-8}	6.9×10^{-3}	0.32	0.24
362	1/12	gr	175	35.6	7×10^{-11}	8.1	0.66	0.28
363	1/24	gr	RT	24.4	4×10^{-11}	4.5×10^{-3}	0.48	0.28
410	1/18	rf	RT	—			0.1	—
411	1/18	gr	RT	—	1×10^{-6}	7.2×10^{-3}	0.23	0.20
412	1/12	gr	RT	—	6×10^{-10}	4.4×10^{-4}	0.35	0.24
413	1/12	rf	RT	—	2×10^{-11}	2.2×10^{-3}	0.48	0.32

The variations of E_σ and σ_{300} with germanium content are drawn in Fig. 2 and Fig. 3 respectively. The figures include a set of data, from reference [6], for thermally evaporated films for comparison. It is obvious from the results that these parameters are not systematic with the Ge content of the PECVD samples, while a more systematic relation has been observed for TE layers. In Fig. 2 the activation energy for TE films never drops below 0.8 eV and shows a maximum of ~1.2 eV at the stoichiometric composition $GeSe_2$, while E_σ never rises above 0.7 eV for all measured

PECVD samples, and does not show any particular trend. The high conductivity values in PECVD films allow measurements around room temperature (300 K). Since this was not possible for TE layers, they are compared in Fig. 3 with TE values measured at 400 K. While σ values in PECVD films are spread over a range of nine orders with no apparent trend, the TE values change with composition and a minimum is revealed near ~ 40% Ge.

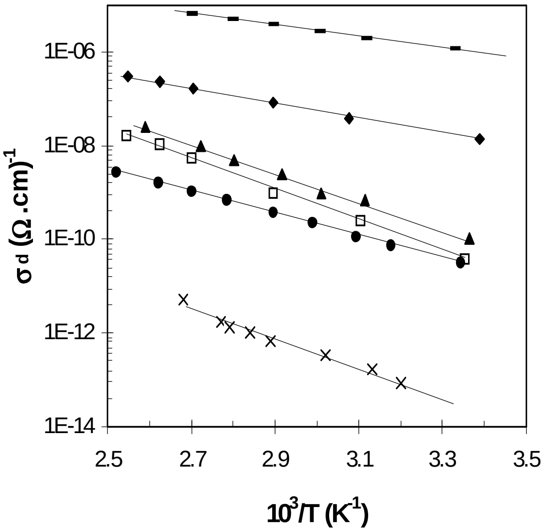

Fig. 1. Electrical dark conductivity temperature dependence for PECVD samples, the (×) represents sample 333, (◊) 348, (◆) 361, (□) 362, (–) 411 and (●) 363 respectively.

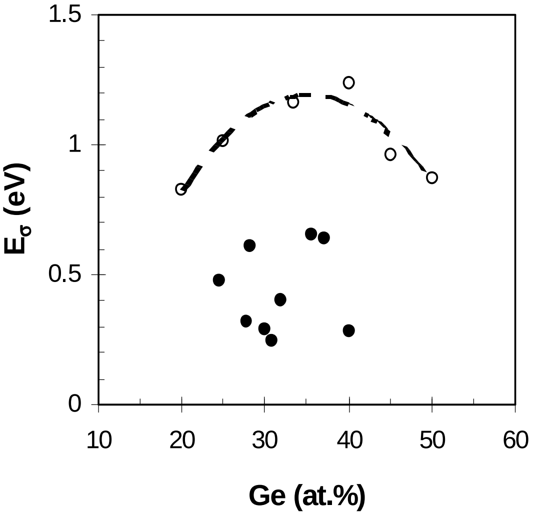

Fig. 2. Activation energy, E_σ, of the dark conductivity vs. Ge content for PECVD samples (full symbols) and evaporated layers (open symbols).

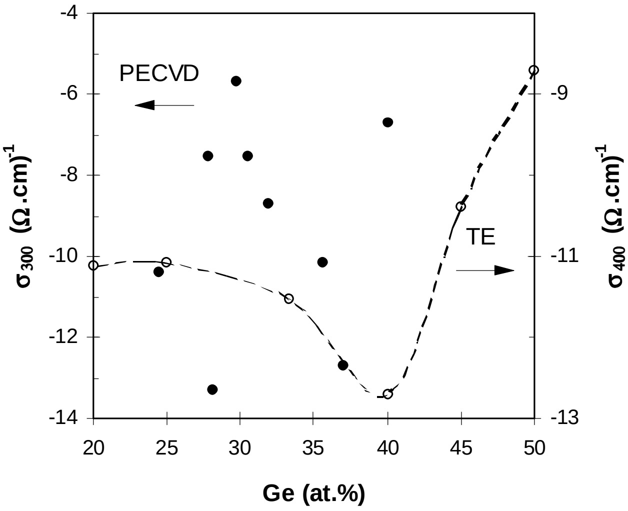

Fig. 3. Conductivity vs. Ge content for PECVD Ge_xSe_{100-x} at 300 K (full symbols), compared to that for TE layers at 400 K (open symbols).

A relationship between σ_0 and the activation energy E_σ, the so called Meyer-Neldel relation (MNR) [8] $\sigma_0 \propto \exp(E_\sigma/E^*)$, is widely seen in disordered semiconductors. It is observed in many activated processes including time-dependent transport behaviour, as well as steady-state properties such as conductivity. Fig. 4 shows MNR for PECVD and evaporated samples. While the data for TE layers of a-Ge-Se (from reference [7]) shows a nice fit to the MNR rule, PECVD data are scattered in a wide range of the graph with no trend to be found among them.

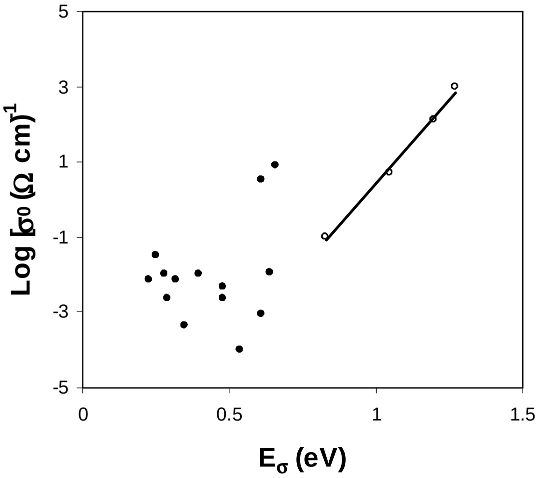

Fig. 4. Measured values of the conductivity prefactor σ_0 versus the conductivity activation energy E_σ, showing the Meyer-Neldel relation for PECVD samples (full symbols) and for evaporated layers (open symbols).

4. Steady-state photoconductivity

4.1 Temperature dependence

Representative photoconductivity data as a function of temperature for PECVD films are shown in Fig. 5; their corresponding dark current measurements are shown in Fig. 1. In general an exponential decrease with temperature is revealed, sometimes with high uncertainty for the activation energy, depending on sample quality. Comparing the ratio photocurrent/dark current (i.e. the photosensitivity I_{ph}/I_d) between TE and PECVD samples, one observes that low photosensitivity generally characterizes PECVD samples. The relative photo-insensitivity made it impossible to measure spectrally resolved photocurrents, whence the full spectral range of the lamp, i.e. white light, was used for illumination. To first approximation the values for the activation energy (E_{ph}) - the slopes of the curves in Fig. 5 - are listed in Table 1 for all samples under investigation. E_{ph} values generally vary between 0.2 and 0.3 eV, and their composition dependence are compared with TE ones in Fig. 6. Again there is no systematic relation between Eph and the composition for PECVD films. However, the general trend for E_σ seems to be maintained here in that lower E_{ph} values are obtained with PECVD samples, in particular in the Se-rich films.

Sample 340 shows completely different photocurrent behaviour from all others; it is observed that illumination causes the current to decrease to values smaller than the dark current level, what is known as negative photoconductivity. Details of this phenomenon are described elsewhere [9].

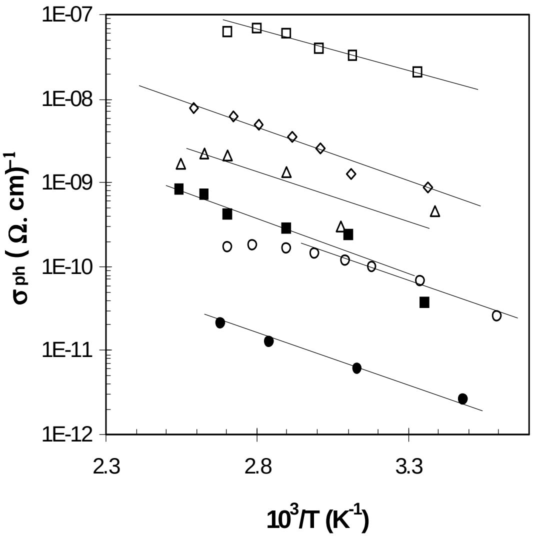

Fig. 5. Temperature dependence of the photoconductivity for PECVD samples, the symbol (●) represents sample 333, (◊) 348, (▵) 361, (■) 362, (□) 411 and (o) represents sample 363. White light was used for illumination.

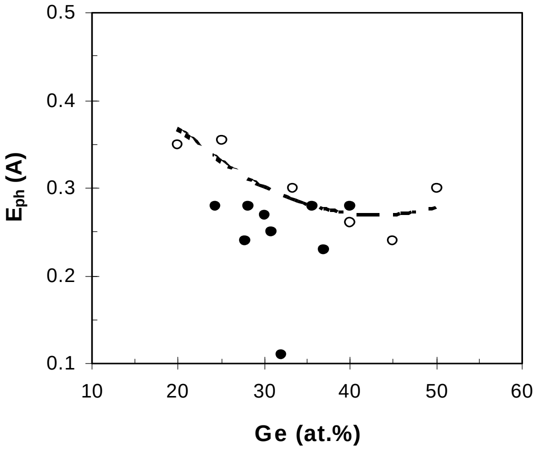

Fig. 6. Activation energy of the photoconductivity as a function of Ge content for PECVD samples (full symbols) and thermal evaporation layers (open symbols).

4.2 Intensity dependence

We also studied the light-intensity dependence of the photocurrents. A typical set of intensity dependence curves in PECVD samples is shown in Fig. 7. It exhibits a power-law relation $I_{ph} \propto I^{\gamma}$, with γ having a constant value around 0.75 at all temperatures. Chalcogenides generally show a change in the value of γ with changing light intensity, indicating a change-over from monomolecular to bimolecular recombination behavior. However, the use of white light for illumination can induce different excitation densities in successive sample depths and thus generate curves with intermediate γ values. But in that case the value of γ is expected to be a function of temperature. About 100 K difference in temperature normally is enough to show differences in γ values, but none are seen in Fig. 7.

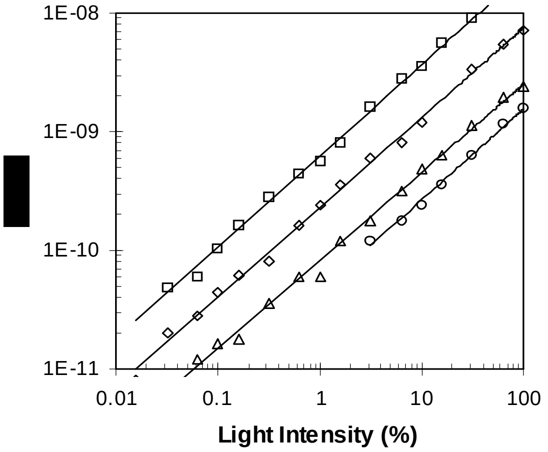

Fig. 7. Light intensity dependence of the photocurrents of sample 347 under white light illumination at T= 382 (□), 341 (◊), 211 (Δ), and 295 K (o).

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5. Discussion

The values for the dark current activation energy E_{σ} in PECVD samples differ drastically from those of samples prepared by TE technique. E_{σ} values, to first approximation, indicate the position of the Fermi energy in the band gap of the materials relative to the conducting band. Generally, in chalcogenides, the Fermi level is located roughly in the middle of the band gap, a situation which corresponds to the data for TE samples where $E_{\sigma} \sim 1.1 - 1.2$ eV for a-$GeSe_2$ and the band gap is in the order of 2.3 eV [10, 11]. However, this is not the case for the PECVD layers. As reported by Sleeckx et al. [7] our PECVD-prepared films do contain up to a few percent of hydrogen at room temperature, mainly bonded to Se atoms, but also to Ge in films which are Ge-rich with respect to the $GeSe_2$ composition. Heat treatment is found to drive out the hydrogen from the material when heated at ~150 °C [12]. However, it is not expected that the hydrogen plays the same role in chalcogenide glasses as it does in tetrahedral coordinated amorphous semiconductors because the defect chemistry in the two materials is different. Here, while the over-all electronic bonding structure remains the same [13,14], the presence of hydrogen may cause some changes in the distribution of localized states in the gap in a way that pushes the Fermi level towards the band edge. Another immediate indication for the changed defect distribution is the appearance of a power-law relation with constant exponent at all temperatures between the photocurrent and the light intensity (Fig. 7) in most PECVD samples, instead of the expected variation in the 1 to 0.5 range. It suggests that the quasi-Fermi level may be shifting in a more or less exponential distribution of localized states, rather than being held in place by the charged defects of the traditional model. It would then follow, in agreement with our observations (Fig. 6), that also E_{ph} should be smaller since that quantity to first approximation then refers to the position of the quasi-Fermi level under illumination. Other consequence of such off-centre location of the Fermi level would be that the measured conductivity itself should be larger (see Table 1) as the occupation probability for the transport states will have increased. It also has to be noted that PECVD films are not only different from others prepared by other techniques, but they also strongly differ among themselves. For example no systematic dependence of the electrical properties upon composition is seen for the PECVD samples, while such relationship always does exist for the TE layers. In addition, it is well known that a collection of differently prepared TE samples can contain different concentration of defects, thereby changing the distribution of gap states, nevertheless a nice exponential relation between σ_0 and E_σ (MNR) does occur. In PECVD samples the presence of hydrogen seems to change the defect distribution such that the observed values of σ_0 vary randomly irrespective of E_σ values.

6. Conclusion

The differences in the dark and photoconductivity behaviours between the PECVD and standard thermal evaporated films raises the question of the way in which the presence of hydrogen has been able to change the defect distribution of the glow-discharge material and neutralizes the negative-U centres which normally pin the Fermi level of the chalcogenides. Both the PECVD material and the TE samples that were used for comparison have been condensed from the gas phase, but obviously from vastly different precursors. So, conceivably, surviving hydrides induce a much larger degree of disorder in the PECVD network.

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