The Determination of Thermal Annealing Effect on a-Si:H Films Coated on Glass and on Single Crystalline of Silicon

Necmi SERİN, Tülay SERİN, Ali Rıza ÖZDEMİR,
Bora ALKAN, Çelik TARIMCI and Basri ÜNAL
Department of Engineering Physics, Science Faculty of Ankara University,
06100 Ankara-TURKEY
e-mail: nserin@eros.campus1.ankara.edu.tr

Abstract

The aim of this study was to examine the effect of thermal annealing on hydrogenated intrinsic amorphous silicon a-Si:H films. Hydrogenated intrinsic amorphous films were seperately coated on glass and single cyrstalline silicon substrates by means of d.c. magnetron sputtering technique. a-Si:H/glass and a-Si:H/c-Si samples were annealed in the temperature range of 23-250°C, 23-200°C and 600-1050°C, respectively. The effect of annealing on the a-Si:H films were examined by means of Infrared vibrational transmittance spectrum technique (IR) in the wavenumber range 4000-400 cm^{-1} and Scanning Electron Microsope (SEM). The results were interpreted in terms of hydrogen diffusion.

1. Introduction

Photodetectors and their characteristics are of great importance since they are very commonly used in the chain of optical data transmission systems. Low current, high response speed and power linearity are the main properties needed in a good photodedector system. The metal/semiconductor/metal type photodedector usually has better performance and simpler processing requirements than those of the conventional and well-established p-i-n photodiodes [1]. Thus metal/semiconductor/metal type photodedector is a good candidate for optical electronic integrated circuit receivers [2-4]. Investigations on the new metal/semiconductor/metal photodedector have been mainly based on III-V compounds [5] or hydrogenated amorphous silicon (a-Si:H) semiconductor materials [6-7].

a-Si:H exhibits several advantages, such as high dark resistance and absorption coefficient, short carrier life-time, low-temperature deposition process, low-cost and easy integration with Si based integrated circuits. But it lacks long-range periodicity and the thermal annealing affects the electrical characteristics of metal/a-Si:H/metal structure [8-9]. Since the response spectrum of a-Si:H is essentially within the visible range, it is not suitable for operating at 830 nm for short-haul optical fiber communication.

The coupling of metal/semiconductor/metal photodedectors made of III-V group into Si-based integrated circuits is difficult. Recently, it was found that metal/semiconductor(c-Si)/metal operated at 830 nm wavelength and were compatible with Si-based integrated circuit technology. However, there is need to improve the performance of c-Si devices since conventional metal/semiconductor/metal photodedectors made of c-Si usually have large dark current, low responsivity and long transient tail. It was hoped that intrinsic amorphous silicon (a-Si:H) overlayer employed instead of c-Si will overcome these difficulties. Development has produced specimens with a low dark-current density of 0.69 pA/μm^2 and a full-width at half-maximum of

55 ps for its temporal response [10]. Thus it was found that a-Si:H formed a good hetereojunction with c-Si[11-12] and improved the performance of solar cells and hetereojunction bipolar transistor.

The present work investigates the effect of thermal annealing on a-Si:H layers coated on glass and single crystaline silicon substrate. a-Si:H/glass and a-Si:H/c-Si samples were fabricated, annealed at various annealing temperatures, and examined for changes in infrared vibrational spectra (IR) and scanning electron microscopy (SEM) images.

2. Experimental details

Hydrogenated intrinsic amorphous silicon films were prepared with the following properties: thickness 1.06 μm, dark electrical conductivity σ_d=7.9 x10^{-13} Ω^{-1}cm^{-1}, photoconductivity σ_{ph}= 7.5x10$^{-7}\Omega^{-1}$cm^{-1}, concentration 6.5x10^{16} cm^{-3}, Urbach energy E$_{rb}$ = 69 meV, and C$_H$=14 (the total hydrogen content in amorphous silicon). Each were separately coated on glass substrate and c-Si crystal substrate in < 111 > orientation by means of d.c. magnetron sputtering technique.

The transmittance response of a-Si:H/glass samples were measured by means of infrared spectrometer in the wavenumber range of 4000-400 cm^{-1}. These samples were annealed at the temperatures of 100, 130, 150, 175 and 200 and 250°C (see Figure 1). The transmittance response of these samples were subsequently measured after each annealing process. The samples of a-Si:H/c-Si were also annealed at the temperatures of 600, 750, 900 and 1050°C. All annealing processes were carried out room atmosphere for a period of 15 minutes. The samples were cooled to room temperature after each annealing process. In order to determine the effect of thermal annealing carried out at room atmosphere in a-Si:H layer, a-Si:H/glass and a-Si:H/c-Si, samples were examined by means of Scanning Electron Microscope (SEM) at 20 KV before and after the annealing processes (see Figures 2-3).

3. Results and discussion

Infrared vibrational spectra (IR) measurements were carried out on these a-Si:H/glass samples annealed in the temperature range 23-250°C. The showed that the transmission characteristics had four absorbances at 3591 cm^{-1}, 2723 cm^{-1}, 2493 cm^{-1} and 1800 cm^{-1}(see Figure 1). It was also observed that there was no effect of thermal annealing on these absorbance lines and their intensities. The most significant observation in our infrared vibrational spectra was the occurrence of new absorbance regions at 2365 cm^{-1}and 2340 cm^{-1} associated with thermal annealing above 100°C annealing temperature. The intensity of these absorbance lines increased with increasing annealing temperature, reached maximum value at 175°C annealing temperature and then decreased, disappearing above 250°C annealing temperature. Our annealing experiments showed that the positions of these lines in infrared vibrational spectra did not shift due to thermal annealing as previously indicated by other authors [13]. No changes were observed on band stretching (SiH$_2$O, around 2180 cm^{-1}) and on band bending (SiH$_2$, at 850 cm^{-1}).

In comparing the above results with those of Parson [14], Tsu [15], Oguz [16], Reimer [17] and John [18] we find the following main differences. In our case the range of IR spectra, the annealing temperature range for a-Si:H/glass samples and the annealing period were 4000-400 cm^{-1}, 25-250°C and 30 minutes, respectively, while in Reimer's and John's studies the IR spectra range, annealing range and annealing period were 2200-500 cm^{-1}, 2400-400 cm^{-1}, 150 - 600°C (at 265, 310 and 390°C, under nitrogen atmosphere) and two hours, respectively. In Oguz's study it is indicated that the PL peak shifts monotically to lower energy with increasing annealing temperature, whereas such behavior was not seen in our data. Other differences can be seen in the apperance of the IR spectra. Under close examination it can be seen that our IR spectra has some significant differences from the IR spectra given in literature. We think the source of this is the different methods used in the preparation of a-Si:H films. The occurrence of absorbance minima at 2365 cm^{-1} and 2340 cm^{-1} thermal annealing in the temperature region 100-200°C can be explained by means of changes in paramagnetic defect densities and evolution of hydrogen accompanied by the changes in Si:H vibrational spectra [2,3]. For this argument it can be said that (i) hydrogen diffusion occurs in the dilute phase coincident with the paramagnetic center density reduction, (ii) the hydrogen transfer from the heavily clustered to the dilute phase occurs at the onset of evolution, and (iii) evolution at low temperatures

($<400°$C) occurs exclusively from the heavily clustered phases independent of the species identified from vibrational spectrocopy as being reduced in density by annealing [17]. John [18] found that during the annealing process, a small degree of oxidation occured due to exposure of the sample to air. As a result two lines in infrared vibrational spectra at 2180 cm^{-1} and at 2240 cm^{-1} were created. It was understood that the bands at 2180 cm^{-1} and 2240 cm^{-1}were derived from SiH_2O and SiH_2O_2 complexes which were formed due to thermal annealing. in our work also, the thermal annealing prosess at room atmosphere causes oxidation of the a-Si:H film, with transmittance absorbance at 2365 cm^{-1} and at 2340 cm^{-1} which indicates that more complex forms of SiH_2O and SiH_2O_2 compounds are formed in the a-Si:H film in the annealing temperature range 100 -200°C.
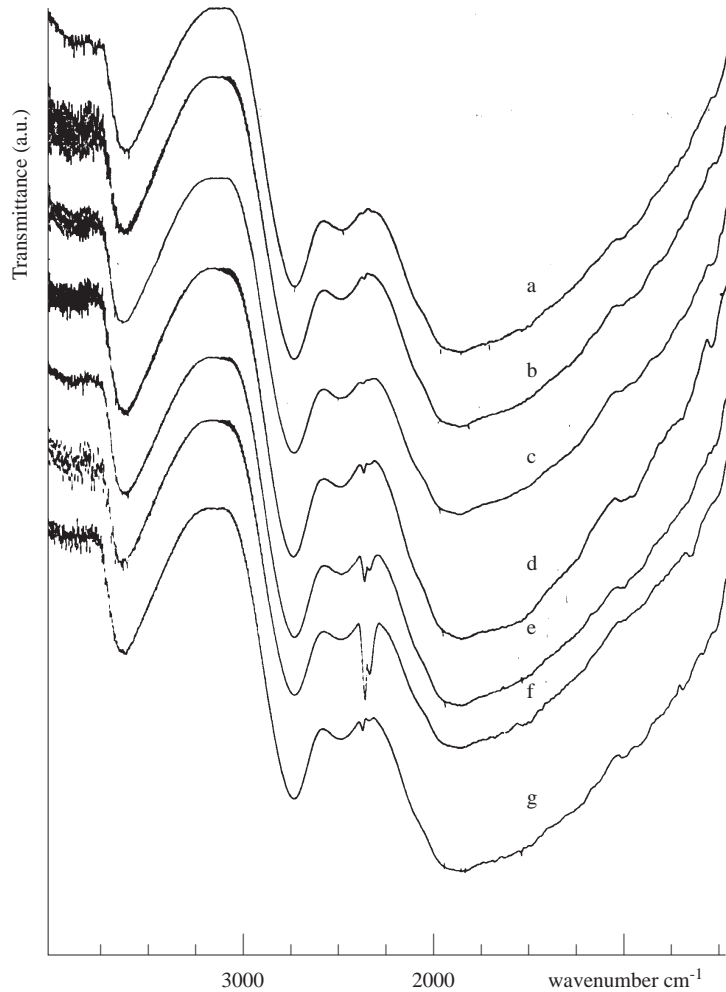
Figure 1. IR spectra of a-Si:H film on glass substrate versus wavenumber at annealing temperatures a) 23°C, b) 100°C, c) 130°C, d) 150°C, e) 175°C, f) 200°C and g) 250°C .

Scanning electron microscope (SEM) measurements (20 kV, mag. 600) were carried out on both a-Si:H/glass and a-Si:H/c-Si samples. For the a-Si:H/glass, annealing in the temperature range 23 - 200°C did not create significant changes in visual observation. When the SEM photographs are carefully examined partial clusters are seen on the film the sample annealed at 23°C. After annealing at 100°C, each cluster split into two. This was explicitly observed at annealing temperature 175°C and the split process was highly developed at annealing temperature 200°C (see Figure 2). Above 200°C no significant change was observed. Annealing above 250°C was not applied since the glass substrates deformed at higher temperature.
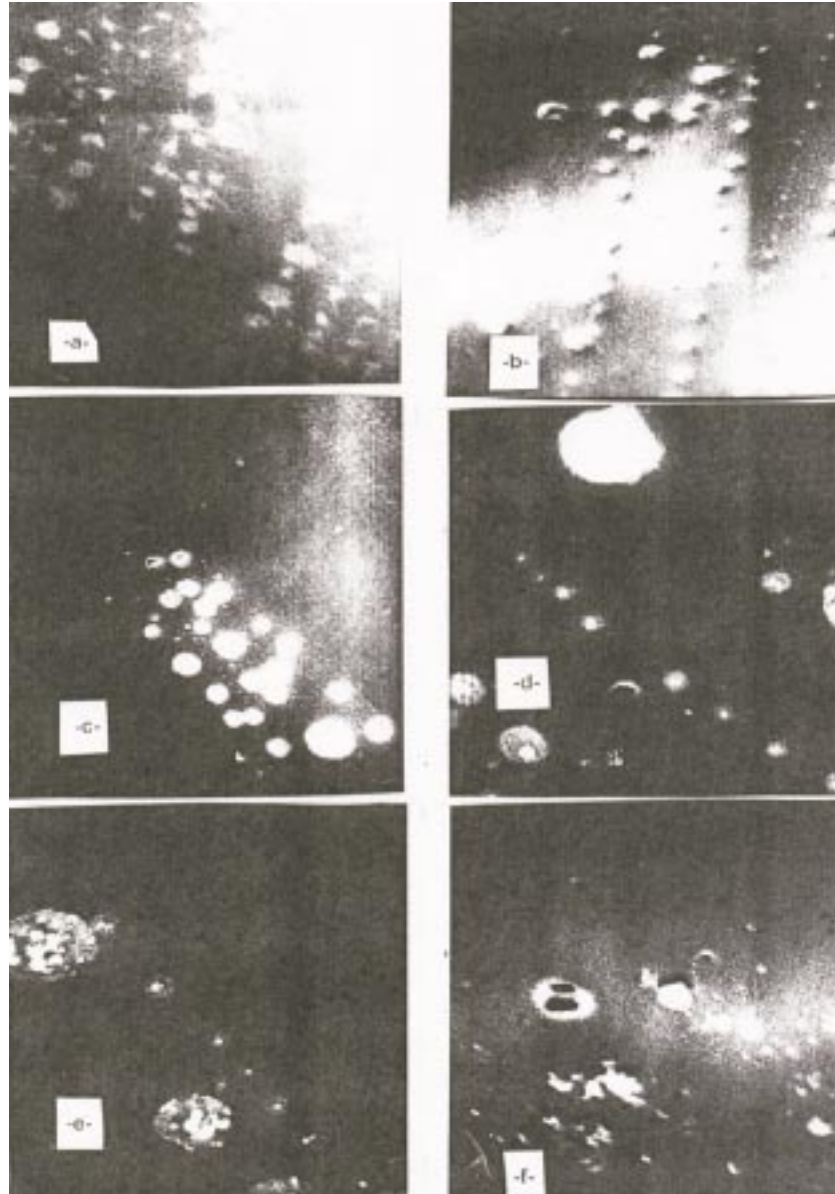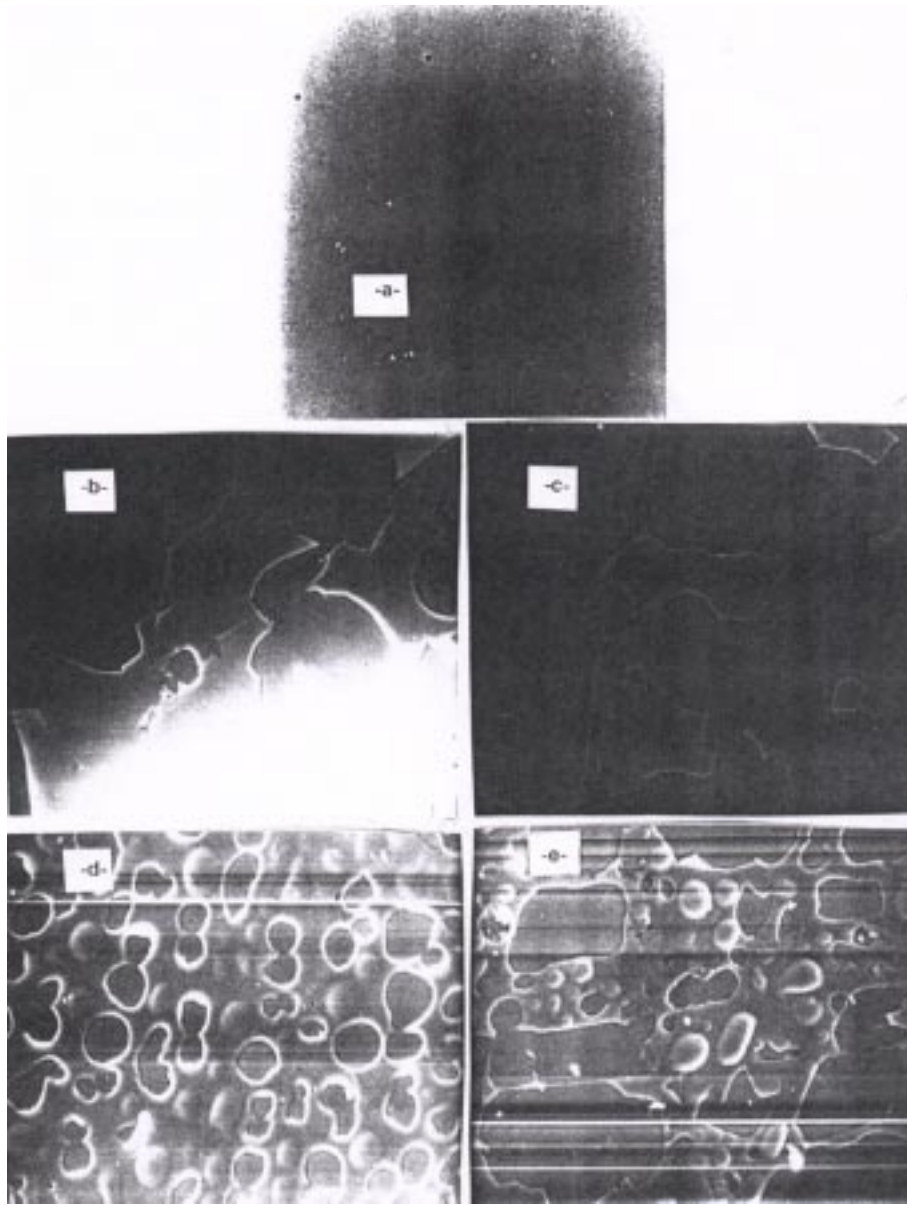
Figure 2. Scanning electron microscopy images of a-Si:H/glass sample at annealing temperatures a) 23°C, b) 100°C, c) 130°C, d) 150°C, e) 175°C and f) 200°C.

In the a-Si:H/c-Si case, SEM measurements carried out on samples annealed in the temperature range 150-175°C also showed the generation of clusters. In the annealing temperature range 200-600°C, no significant changes were observed (see Figure 3). As seen from a SEM photograph of a sample treated at 600°C, some deformations began on parts of the a-Si:H film which lied on single crystals of silicon (see Figure 4). The deformation of the a-Si:H layer was increased when the annealing temperature rose to 750°C. A more regular form resembling crystallization was obtained at annealing temperature 900°C, but this topological form was lost at annealing temperature 1050°C. These results were compared with the annealing experiments of Ruttensperger [19], who performed the process in the range 500-1400°C (at temperature values 800, 1100, 1200, 1350°C) using a-SiC:H films prepared by plasma deposition onto [1011] crystal surface of sapphire (Al_2O_3). He investigated the effect of annealing by measuring optical transmission and reflection and via spectroscopic techniques such as photo-thermal deflection (PDS), infrared vibration (IR), Auger electron (AES) as well as gas evolution optical and scanning electron microscopy (SEM). He claimed that, as in

the case of a-Si:H, H_2 evolved from the a-SiC:H films in two steps with the diffusion maximum occuring at around 550 and 900°C. IR analysis on step-wise annealed films revealed that H was first removed from SiH_n sites, then from CH_n sites. These H-evolution processses were accompanied by a reduction of the Tauc optical gap from about 2.4 to 1.8 eV for a-SiC:H and a significant broadenning in the Urbach tail resulted. Upon crystallization the brownish high temperature annealed a-SiC:H films transformed into a transparent poly-crystalline states. In Ruttensperger's work, crystallization began at around 1000°C and completed at 1250°C while in our study it occurred at around 900°C. Under Ruttensperger's view we can explain the deformation that occured at annealing temperature range 600-1050°C as being a H-evolution processes accompanied by a reduction of Tauc optical band.
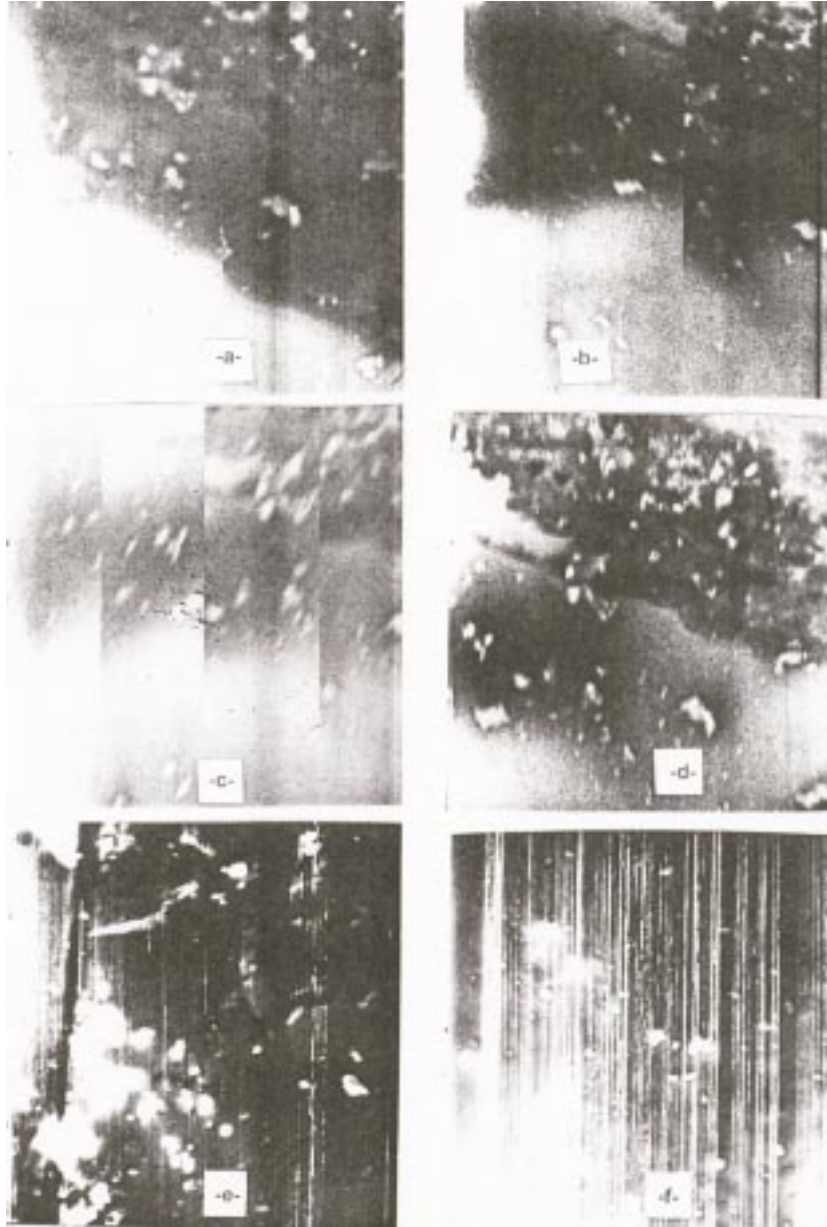
Figure 3. Scanning electron microscopy images of a-Si:H/c-Si sample at annealing temperatures a) 23°C, b) 100°C, c) 130°C, d) 150°C, e) 175°C and f) 200°C.

Figure 4. Scanning electron microscopy images of a-Si:H/c-Si sample at annealing temperatures a) 23°C, b) 600°C, c) 750°C, d) 900°C and e) 1050°C.

Thus from the infrared vibrational spectra of a-Si:H/glass and the photographs of Scanning electron microscope (SEM) belonging to a-Si:H/glass and a-Si:H/c-Si, there is explicit indication that thermal annealing processes carried out in the annealing temperature range 23-250°C and 600-1050°C created significant changes in the hydrogeneted amorphous silicon films. These changes were explained by means of hydrogen evolution due to thermal annealing in a-Si:H film.

Acknowledgments

References

[1] L. D. Rogers, *Lightwave Technol.,* **12** (1991) 625

[2] J. S. Wang, C. G. Shih, W . H. Chang, J. R. Middleton, P. J. Apostolakis and M. Feng, *IEEE Photo. Technol. Lett.,* **5** (1993) 316

[3] G. K. Chang, W. P. Hong, J. L. Gimlett, R. Bhat, C. K. Nguyen, G.Sasaki and J.C. Yong, *IEEE Photo. Technol. Lett.,* **2** (1990) 197

[4] C.S. Harder, B Van Zeghbroeck, H. Meier, W. Patrick and P. J. Vettiger, *Lightwave Technol.,* **9** (1989) 171

[5] H. Schumaacher, H. P. Leblanc, J. Soole and R. Bhat, *IEEE Electron Device Lett.,* **11** (1988) 607

[6] L. H. Laih, Y. a. Chen, W. C. Tsay and J. W. Hong, *IEEE Electronic Lett.,* **10** (1996) 929

[7] L.H. Laih, W. C. Tsay, Y. A. Chen, T.S. Jen, R. H. Yuang and J. W. Hong, *IEEE Electronic Lett.,* **31** (1995) 2123

[8] N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials (Oxford University Press, 2nd ed.)(1979) Chap.6

[9] T. Serin, Semicond. *Sci. Technol.,* 12 (1997) 291

[10] H. Mimura and Y. Hatamaka, *J. Appl. Phys.,* **61** (1987) 7

[11] M. M. Rahman and S. Furukawa, *Jpn. Appl. Phys.,* **23** (1984) 515

[12] K. Okuda, H. Okamoto and Y. Hamakawa, *Jpn. J. Appl. Phys.,* **22** (1983) L603

[13] M.Niwano, M. Teroski and J Kuku, *Surface Science,* **420/1** (1999) 6

[14] G.N. Parsons, C. Wang and G. Lucovsky, *Thin Solid Films* **193** (1990) 577

[15] D.V. Tsu and G. Luovsky, *Journal of Non-Crystalline Solids,* **97-98** (1987) 839

[16] S. Oguz, R. W. Collins, M. A. Presler and W. Paul, *Journal of Non-Crystalline Solids* **35-36** (1980) 231

[17] J. A Reimer, R.W. Vaughan, J. C. Knights, *Solid State Communications,* **37** (1981) 161

[18] P. John B. C. Cowie and I. M. Odeh, *Philosophical Magazine B,* **49** (1984) 559

[19] B. Ruttensperger, G. Krötz, G. Müller, G. Derst and S. Kalbitzer, *Journal of Non-Crystalline Solids,* **137-138** (1991) 635 (1993) 635