Thermal stability of the optical band gap and structural order in hot-wire deposited amorphous silicon

C. J. Arendse[1], G. Malgas[2,*] C. J. Oliphant[1, 2], T. F. G. Muller[1] and D. Knoesen[1]

[1] Department of Physics, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

[2] National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, P. O. Box 395, Pretoria 0001, South Africa

Abstract

The material properties of hydrogenated amorphous silicon (a-Si:H) have been known to change when exposed to elevated temperatures. In this work we report on the thermal stability of the optical band gap and structural disorder in hot-wire deposited a-Si:H with different hydrogen concentrations. Furthermore, the changes in the structural disorder will be correlated with the changes in the optical band gap. Raman spectroscopy shows evidence that no crystallization is induced at 450 °C and that the structural disorder increases upon annealing. The increase in the structural disorder results in a broadening of the valence and conduction band tails, thereby pinning the valence and conduction band edges closer together, resulting in a decrease in the optical band gap as probed by optical reflection and transmission measurements.

[*] Corresponding author: Dr. Gerald Malgas. Tel: (012) 841 3972; Fax (012) 841 2229
E-mail: GMalgas@csir.co.za

Keywords

Hot-wire CVD, Crystallization, Raman spectroscopy, Optical band gap

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has proven to be of technological importance in applications such as solar cells, thin film transistors and liquid crystal displays [1-3]. However, a major concern of a-Si:H is the fact that the stability of the material degrades when it is exposed to prolonged sunlight illumination [4]. Furthermore, in the manufacturing of solar cells the intrinsic a-Si:H layer is usually subjected to further heat treatments, e.g. the post-deposition of the n- or p-doped layers. Moreover, in subsequent use the solar cells may also be exposed to temperature cycling over a wide range of temperatures.

It has been shown that both the hydrogen concentration and structural disorder in a-Si:H are critical factors which eventually determines the stability of the material [5]. The optical band gap of a-Si:H is one of the most widely studied subjects in solar cell applications, since it is related to the electronic structure of the material and, more importantly, since the efficiency of solar cells made from this material is directly related to it. It is generally accepted that the band gap is dependent on both the hydrogen concentration and the structural disorder [6-10].

In this work we investigate the effect of isochronal annealing on the structural disorder and optical band gap of hot-wire deposited a-Si:H with different hydrogen concentrations.

Additionally, the changes in the structural disorder will be correlated with the changes in the optical band gap.

2. Experimental Details

The a-Si:H samples were deposited simultaneously on single-side polished <100> crystalline silicon (c-Si) and Corning 7059 substrates by the hot-wire CVD process [11] in an MVSYSTEMS deposition chamber [12], where SiH_4-gas is decomposed by the catalytic action of seven parallel tantalum wires at a temperature of 1600 °C. The substrate-to-filament distance and the separation distance between the wires amounted to 18 mm and 15 mm, respectively. The deposition conditions of the samples are given in Table 1.

Isochronal annealing was performed under high-purity, flowing argon gas in a tube furnace. The samples were annealed subsequently at annealing temperatures (T_A) ranging from 150 – 450 °C in 50 °C increments with a total annealing time of 30 minutes for all temperatures. The ambient temperature at the sample position in the experimental set-up amounted to 21 °C.

Fourier transform infrared spectroscopy (FTIR) measurements were performed in transmission mode on the samples deposited on c-Si, using a DIGILAB FTS-40 FTIR spectrophotometer equipped with a liquid-nitrogen-cooled HgCdTe detector. The hydrogen content was calculated from the integrated absorption of the rocking modes of ≡Si–H, $(=Si=H_2)_n$ and $-Si\equiv H_3$ using the procedures of Brodsky et al [13] and proportionality constant proposed by Shanks et al [14]. The error in the results is estimated to be within 15%.

Raman spectroscopy measurements were performed in reflection mode on the samples deposited on Corning 7059, using the 514.5 nm line of a Spectra Physics Ar^+-ion laser. A detailed description of the Raman experimental set-up is described elsewhere [15]. The transverse-optical peak (TO) in the vibrational density of states of amorphous silicon reflects the degree of disorder in the amorphous network [16].

Optical reflection and transmission measurements were performed in the energy range 1.2 – 2.4 eV with an energy resolution of 3 meV. These measurements were used to calculate the sample thickness, refractive index and absorption coefficient, using the method proposed by van den Boogaard [17].

3. Results and Discussion

The Raman spectra of samples A and B in the as-deposited and final annealing states are shown in Fig. 1 and 2, respectively. The spectra were normalized to the height of the a-Si TO-peak. No emerging c-Si TO-peaks are observed at ~ 520 cm^{-1} before and after annealing, illustrating that no amorphous-to-crystalline phase transitions occur in both samples as annealing progresses. Further annealing of both samples up to 550 °C induces no detectable phase transitions. This is consistent with the observations of Spinella et al [18] who have shown that crystal grain nucleation in a-Si occurs at temperatures above 560 °C.

The plot of the half-width-half-maximum (HWHM) of the a-Si TO-peak ($\Gamma/2$) as a function of annealing temperature for samples A and B is shown in Fig. 3. There exists a linear relationship between $\Gamma/2$ and the average bond angle variation $\Delta\vartheta_b$ [16]. In the as-deposited state the $\Delta\vartheta_b$-value for samples A and B amounts to 7.28° and 8.03°, respectively. The $\Delta\vartheta_b$-value of sample A is among the lowest determined for device-quality HW-deposited a-Si:H [19], illustrating the superior structural quality of this sample. Annealing sample A at temperatures up to 300 °C induces no considerable change in $\Gamma/2$ followed by an increase for $T_A \geq 350$ °C. An increase in $\Gamma/2$ is observed for sample B at $T_A \geq 300$ °C. The increase in $\Gamma/2$ is associated with an increase in the structural disorder, caused by the creation of unterminated Si dangling-bonds [20] (see Fig. 4).

The optical band gap E_g was determined from the absorption coefficient (α) and the refractive index (n) using the Tauc-convention [21], by extrapolating $[\alpha(E)n(E)E]^{1/2}$ to $\alpha(E) = 0$ for $\alpha(E) \geq 10^3$ cm^{-1}. The optical band gap as a function of annealing temperature for samples A and B is shown in Fig. 5. After annealing samples A and B at 350 °C and 300 °C, respectively, a decrease in E_g is observed. It should be noted that similar trends in the cubic band gap for samples A and B were observed, using the method proposed by Klazes et al [22].

Müller et al [23] have shown that the slope of the linear fit (B_g) through $[\alpha(E)n(E)E]^{1/2}$ is proportional to the density of states in the valence and conduction band tails. Fig. 6 shows the plot of B_g as a function of annealing temperature for samples A and B. Similar trends in E_g and B_g are observed with increasing annealing temperature, suggesting that the decrease in B_g is associated with the broadening of the valence and conduction band tails, thereby pinning the

valence and conduction band edges closer together resulting in a reduction in E_g. The broadening of the valence and conduction bands is caused by an increase in the structural disorder, as seen by the increase in $\Gamma/2$ (Fig. 3). Therefore we conclude that the decrease in the band gap is a direct result of the increase in the structural disorder.

4. Conclusion

Raman spectroscopy and optical measurements were used to correlate changes in the structural disorder and the optical band gap in HW-deposited a-Si:H subjected to isochronal annealing at temperatures in excess of 150 °C. Our results suggest that no crystallization is induced in both samples at temperatures as high as 550 °C. The structural disorder increases at temperatures above 300 °C, caused by the termination of hydrogen-passivated Si dangling bonds. The increase in the structural disorder results in a broadening of the valence and conduction band tails, thereby pinning the valence and conduction band edges closer together, resulting in a decrease in the optical band gap.

Acknowledgements

The authors would like to acknowledge the financial support of the National Research Foundation of South Africa (GUN. 2050646). The authors also wish to thank Dr. Anke Brockhoff of the Debye Institute of Utrecht University for the Raman spectroscopy measurements.

References

1. A. Madan, M.P Shaw, The Physics and Applications of Amorphous Semiconductors, Academic Press, 1988
2. V. Chu, J. Jarego, H. Silva, T. Silva, M. Reissner, P. Brogueira, J.P. Conde, Appl. Phys. Lett. 70 (1997) 2714
3. H. Meiling, R.E.I. Schropp, Appl. Phys. Lett. 70 (1997) 2681
4. D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292
5. R.A. Street, K. Winer, Phys. Rev. B 40 (1989) 6236
6. A.J.M. Berntsen, Ph.D. thesis, Utrecht University, Utrecht, The Netherlands (1993)
7. K.F. Feenstra, R.E.I. Schropp, W.F. van der Weg, J. Appl. Phys. 85 (1999) 6843
8. K.H.M. Maessen, M.J.M. Pruppers, J. Bezemer, F.H.P.M. Habraken, W.F. van der Weg, Mater. Res. Soc. Symp. Proc. 95 (1987) 201
9. H. Meiling, M.J. van den Boogaard, R.E.I. Schropp, J. Bezemer, W.F. van der Weg, Mater. Res. Soc. Symp. Proc. 192 (1990) 645
10. N. Maley, J.S. Lannin, Phys. Rev. B 36 (1987) 1146
11. H. Wiesmann, A.K. Ghosh, T. McMahon, M. Strongin, J. Appl. Phys. 50 (1979) 3752
12. C.J. Arendse, M.Sc. thesis, University of the Western Cape, Bellville, South Africa (1999)
13. M.H. Brodsky, M. Cardona, J. J. Cuomo, Phys. Rev. B 16 (1977) 3556
14. H. Shanks, C.J. Fang, L. Ley, M. Cardona, F.J. Desmond, S. Kalbitzer, Phys. Status Solidi B 100 (1980) 43
15. A.M. Brockhoff, Ph.D. thesis, Utrecht University, Utrecht, The Netherlands, 2001
16. D. Beeman, R. Tsu, M.F. Thorpe, Phys. Rev. B 32 (1985) 874

17. M.J. van den Boogaard, Ph.D. thesis, Utrecht University, Utrecht, The Netherlands (1992)
18. C. Spinella, S. Lombardo, F. Priolo, J. Appl. Phys. 84 (1998) 5383
19. A.H. Mahan, D.L. Williamson, T.E. Furtak, Amorphous and Microcrystalline Silicon Technology (1997), edited by S. Wagner, M. Hack, E.A. Schiff, R.E.I. Schropp, I. Shimizu Materials Research Society, Pittsburgh (1997), Vol. 467
20. C. J. Arendse, D. Knoesen, D.T. Britton, Thin Solid Films 501 (2006) 92
21. J. Tauc, Optical Properties of Solids, ed. F. Abeles, North-Holland Publ., Amsterdam (1972)
22. R.H. Klazes, M.H.L.M. van den Broek, J. Bezemer, S. Radelaar, Phil. Mag. B 45 (1982) 377
23. G. Müller, H. Mannsperger, S. Kalbitzer, Phil. Mag. B 53 (1986) 257

List of table and figure captions

Table 1 Deposition conditions of the a-Si:H samples.

Fig. 1 Raman spectra of sample A in the as-deposited state (solid circles) and after annealing at 400 °C (open circles).

Fig. 2 Raman spectra of sample B in the as-deposited state (solid circles) and after annealing at 450 °C (open circles).

Fig. 3 HWHM of the a-Si TO-peak as a function of annealing temperature for sample A (solid circles) and sample B (open circles). The lines are guides to the eye.

Fig. 4 HWHM of the a-Si TO-peak as a function of the bonded hydrogen content for sample A (solid circles) and sample B (open circles). The lines are guides to the eye.

Fig. 5 Optical band gap as a function of annealing temperature for sample A (solid circles) and sample B (open circles). The lines are guides to the eye. The lines are guides to the eye.

Fig. 6 The slope of the linear fit though $[\alpha(E)n(E)E]^{1/2}$ as a function of annealing temperature for sample A (solid circles) and sample B (open circles). The lines are guides to the eye.

Table 1

Sample No.	Substrate temperature (°C)	Deposition pressure (Pa)	Silane flow rate (sccm)
A	330	2	60
B	180	8	60

Figure 1

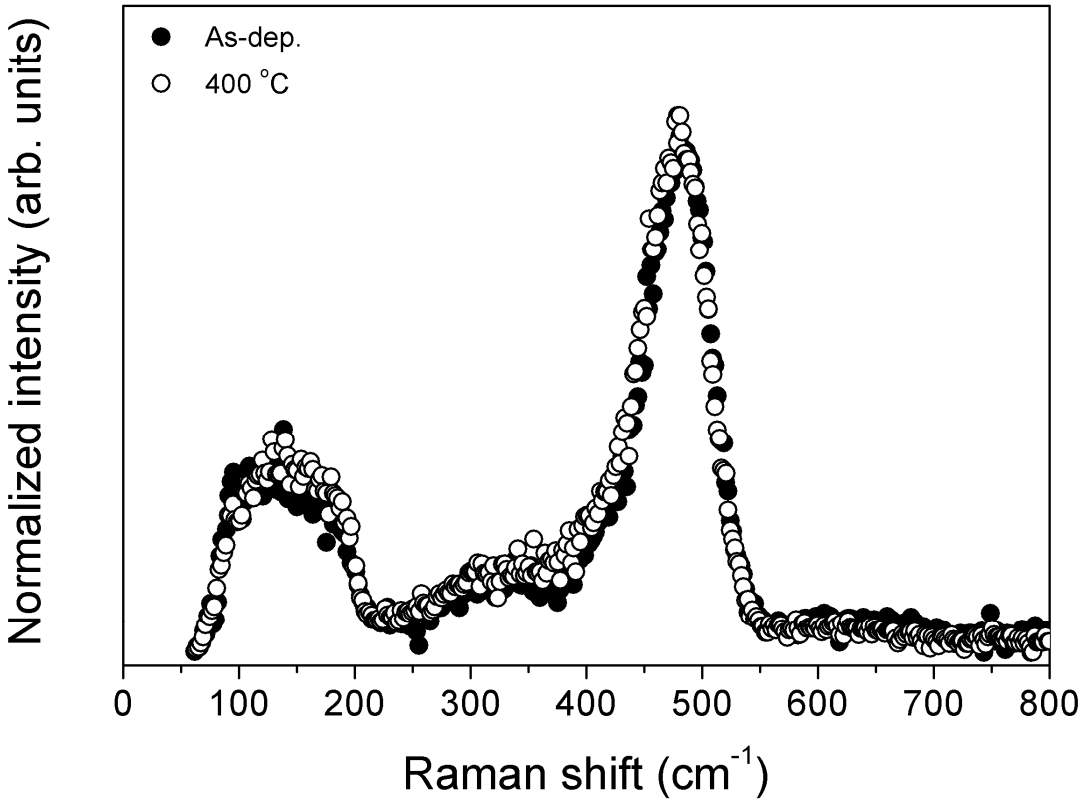

As-dep.
400 °C
Normalized intensity (arb. units)
0
100
200
300
400
500
600
700
800
Raman shift (cm-1)

Figure 2

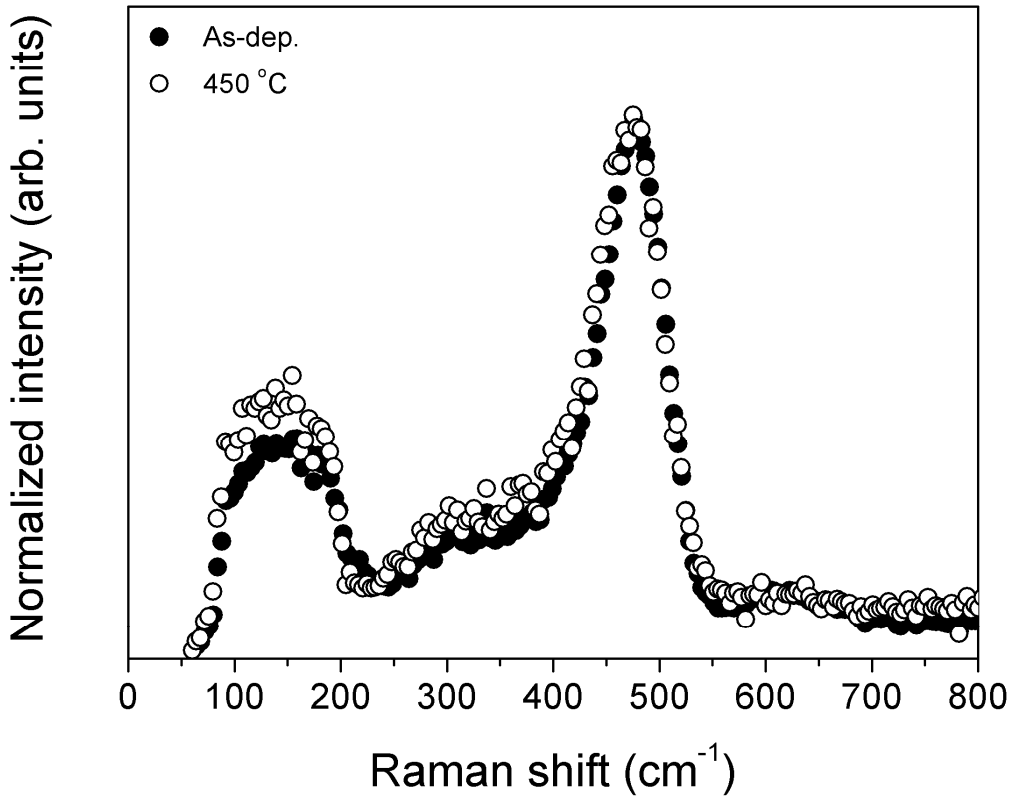

As-dep.
450 °C
Normalized intensity (arb. units)
0
100
200
300
400
500
600
700
800
Raman shift (cm-1)

Figure 3

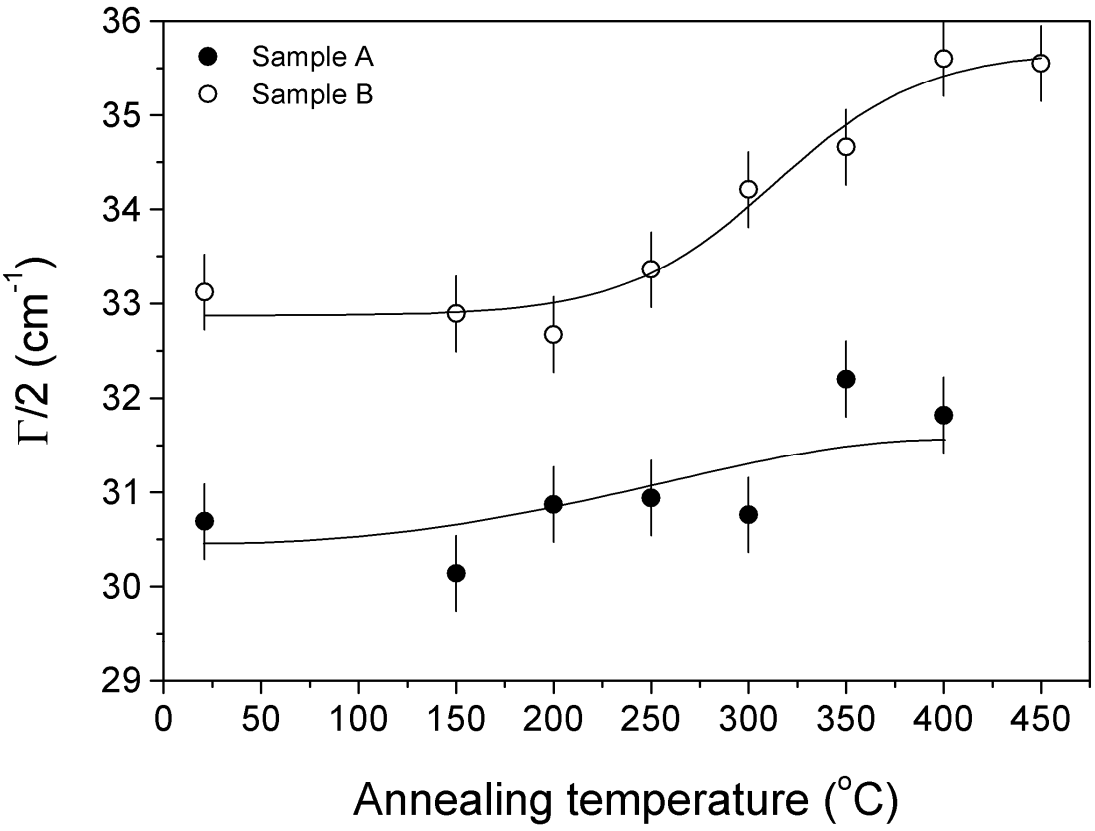

Sample A
Sample B
Γ/2 (cm-1)
Annealing temperature (°C)
36
35
34
33
32
31
30
29
0
50
100
150
200
250
300
350
400
450

Figure 4

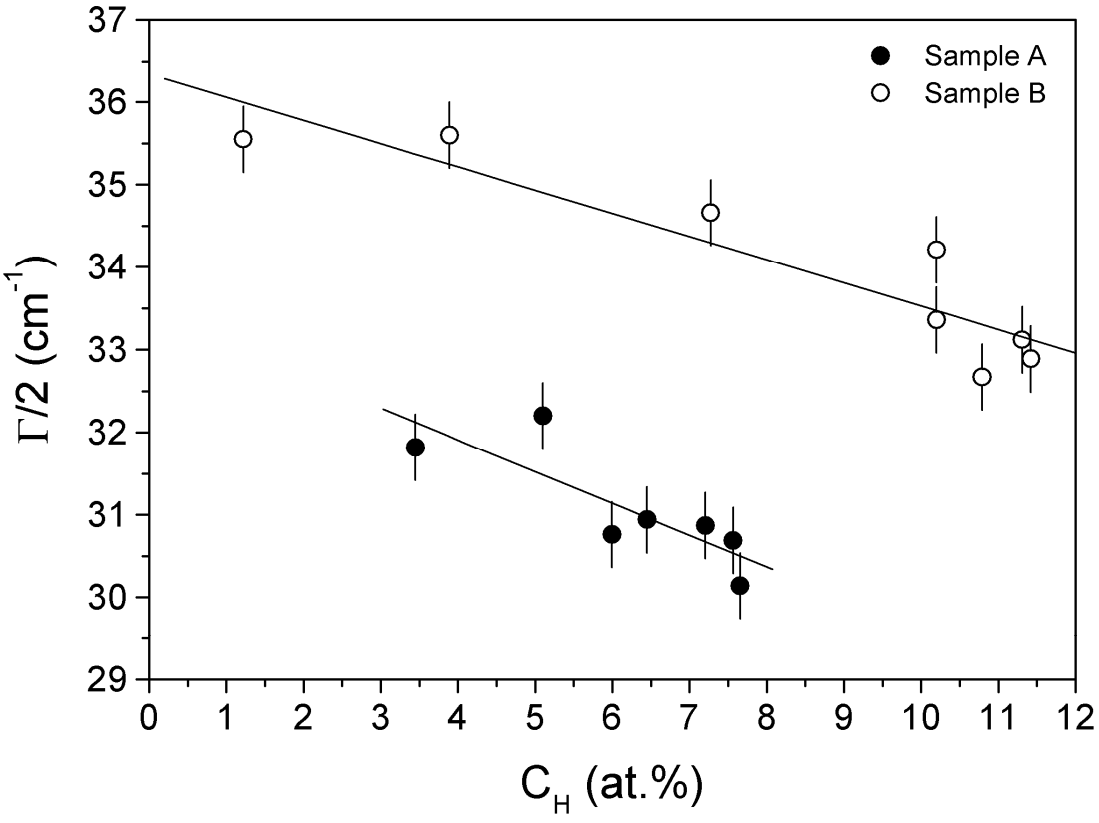

Sample A
Sample B
Γ/2 (cm-1)
CH (at.%)
37
36
35
34
33
32
31
30
29
0
1
2
3
4
5
6
7
8
9
10
11
12

Figure 5

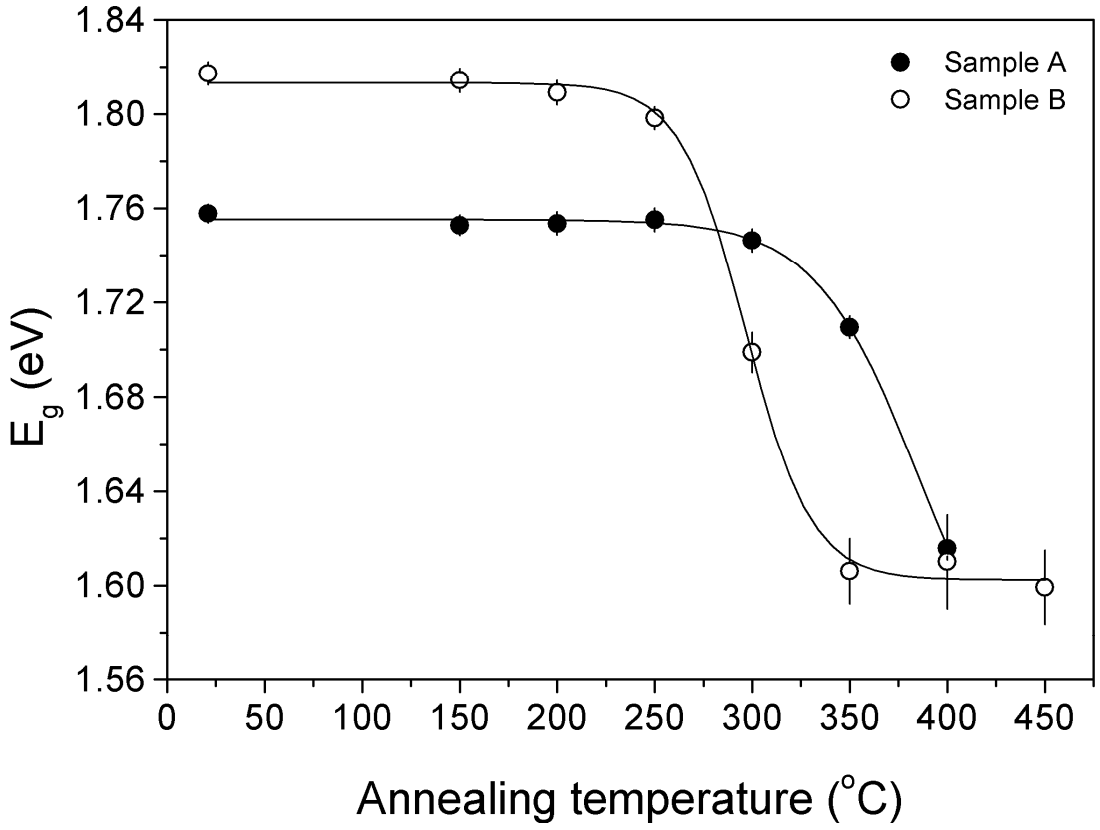
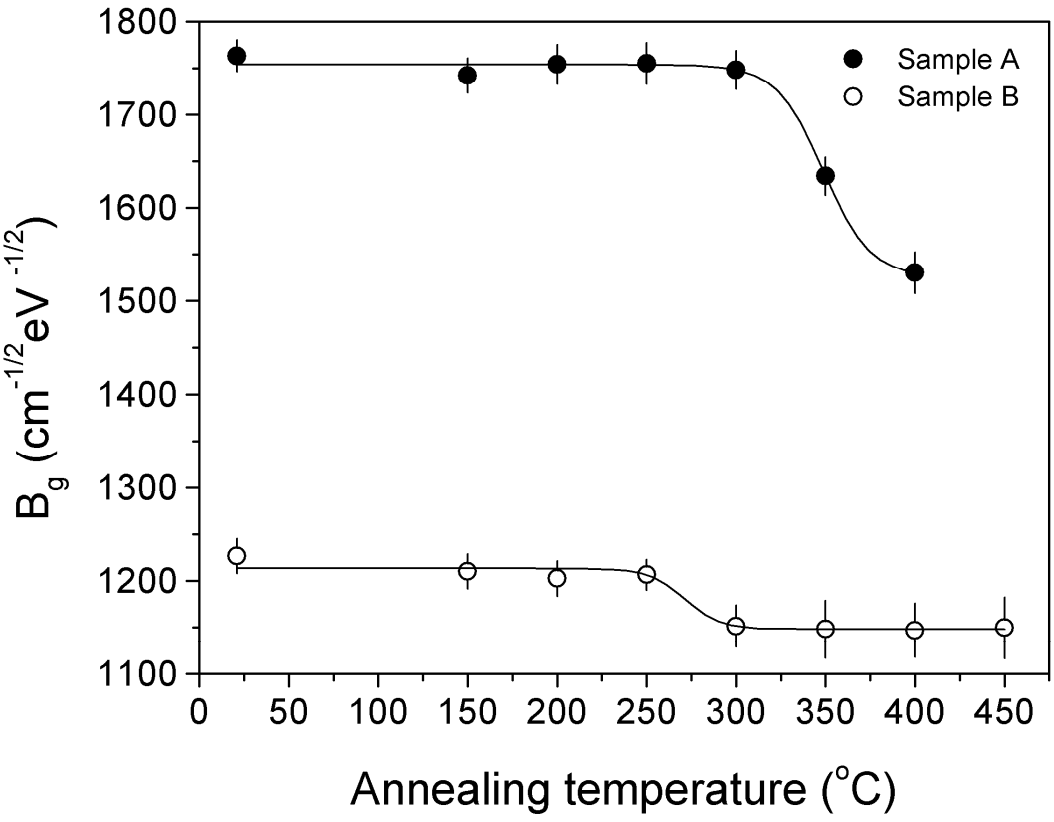

1.84
1.80
1.76
1.72
1.68
1.64
1.60
1.56
E_g (eV)
0
50
100
150
200
250
300
350
400
450
Annealing temperature (°C)
Sample A
Sample B

Figure 6


1800
1700
1600
1500
1400
1300
1200
1100
0
50
100
150
200
250
300
350
400
450
Sample A
Sample B
B_g ($cm^{-1/2}eV^{-1/2}$)
Annealing temperature (°C)