phys. stat. sol. (c) **5**, No. 12, 3776–3779 (2008) / **DOI** 10.1002/pssc.200780109

physica status solidi c
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current topics in solid state physics

Determination of critical points on silicon nanofilms: surface and quantum confinement effects

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Received 10 November 2007, revised 8 May 2008, accepted 13 May 2008
Published online 16 September 2008

PACS 78.20.Ci, 78.66.Db, 78.67.Bf, 78.67.-n

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In this work, we present a comprehensive study of the optical properties of nanocrystalline silicon films with thickness varied from 5 to 30 nm. Spectroscopic ellipsometry is employed to determine the dielectric functions of these films using a structural two-layer model based on the rigorous Airy formula. Our investigation gives an important insight of the origin of critical points for direct and indirect gaps of nanocrystalline silicon films as well as the evolution of them with decreasing the film thickness. The influence of the quantum confinement effect due to the nanoscale grain size and the surface vibrations at the interface on the optical properties are examined in detail.

1 Introduction Polycrystalline Si films extensively used in Microelectronics are fabricated by Low Pressure Chemical Vapor Deposition of Si at high temperature [1]. Crystal size depends on film thickness and it is in the nanometer range when film thickness is reduced down to the nanometer range. Recently, it has been reported [2] that efficient generation of multiple excitons per absorbed photon of energy greater than twice the band gap of silicon nanocrystals (Si-NCs) represents one possible route towards enhanced photon conversion efficiency in solar cell devices. Especially, this multiple excitons generation in nanocrystalline Si at lower photon energies in the visible region has the potential to increase the power conversion efficiency in Si-based photovoltaic cells towards a thermodynamic limit of 44% at standard AM1.5 solar intensity. Furthermore, Si-NCs of sizes 3-6 nm embedded in SiO_2 have been used to fabricate non-volatile memory devices [3] with considerable advantages. However, in spite of this breakthrough effort towards the use of Si-NCs in photovoltaics and memory applications, very few fundamental properties of the band structure of material are well known. In view of this gap in the literature, we have investigated such films of nanocrystalline silicon grown on a quartz substrate and we found that they show interesting optical properties attributed to quantum effects (quantum confinement or Coulomb interactions within nanocrystals). Furthermore, in very thin as-grown nanocrystalline silicon films on quartz [4], the nanograins at the interface are partially surrounded by SiO_2· while those at the surface are also covered by a native oxide formed by exposing the films to the ambient atmosphere. When we decrease the film thickness down to 5 nm, the surface/interface to volume ratio is substantially increased, so the effects due to SiO_2 chemical environment of Si nanograins become important [5].

In this work, we have employed multiwavelength spectroscopic ellipsometry (SE) [6-8] to investigate the optical properties of very thin as-grown nanocrystalline silicon films with thickness in the range of 5-30 nm on a quartz substrate. Our aim is to determine the critical points of the band structure for these very thin nanofilms as well as the influence of the film thickness on their properties. Growth was performed at a temperature of 610 °C and a pressure of 300 mTorr. Transmission electron microscopy and electron diffraction patterns taken in these nanofilms reveal the crystallinity of them with a grain size that is dependent on film thickness [9]. In the z-direction the grain size was approximately equal to film thickness, while in the plane (x-y

directions) it was larger (in the range of 5-19 nm in the case of the 5 nm thick film and in the range of 6-32 nm in the case of the 30 nm film) [10].

2 Experimental results and analysis In Fig. 1, we present the pseudodielectric functions over the photon energy range 1.4 to 5 eV at an optimum incident angle of $\phi = 75^o$ for all films under investigation in this work. Here we should point out that the beam size of the ellipsometer is 2 mm thus the optical functions reveal information for a large distribution of Si-NC sizes. These functions describe the whole material as a homogeneous structure. However, the changes in ellipsometric spectra for different film thicknesses reflect the structural changes of the material due to the formation of grains with nanoscale size. As shown in this figure, the ellipsometric spectra present a strong redshift with increasing the film thickness for both pseudodielectric functions.

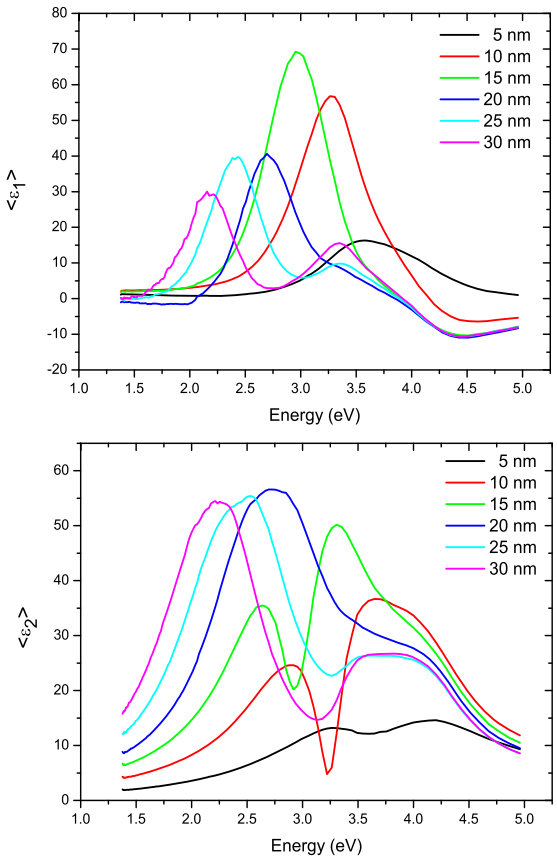

Figure 1 Pseudodielectric functions $<\varepsilon_1>$, $<\varepsilon_2>$ over the photon energy range 1.4 to 5 eV of nanocrystalline silicon films of varying thickness in the range of 5-30 nm on a quartz substrate.

The dielectric functions of quartz substrate have been extracted by bulk calculations of its measured ellipsometric response. In order to analyze the ellipsometric spectra we have utilized a two-layer structural model: the nanocrystalline silicon film with unknown properties as one layer and the quartz substrate with the measured optical response as the second. The optical properties of the unknown layer could be calculated using the Fabry-Perot equations (Airy rigorous model [11]) of multiple reflections between the interfaces. In this model, the incident and total reflected electric field of light could be analytically determined. The ratio between the incident and reflected fields at p and s polarized light give the reflection Fresnel coefficients. Using the ellipsometric parameters tanΨ and cosΔ [11], the thickness, the refractive index (n) and the extinction coefficient (k) of unknown layer onto a known substrate could be determined. n and k can, in term, be used to calculate the dielectric function of nanofilms and consequently their optical properties. Our model is used in a regression process with the nonlinear Levenberg-Marquardt method using a merit function between the measured and the extracted values of ellipsometric parameters [12].

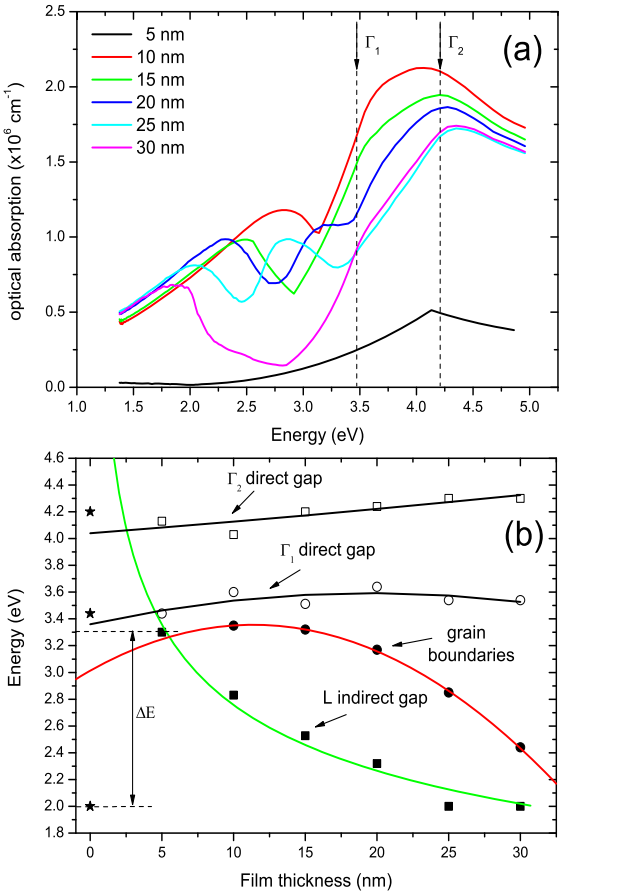

Figure 2 (a) Absorption coefficient over the photon energy range 1.4 to 5 eV of nanocrystalline silicon films of varying thickness in the range of 5-30 nm on a quartz substrate. The dashed lines represent the energy of Γ_1 and Γ_2 critical points in the first Brillouin zone of bulk crystalline silicon. (b) Dependence of critical points of nanocrystalline silicon as a function of film thickness. Star symbols at zero thickness represent the critical points of bulk crystalline silicon for comparison purposes.

Figure 2a shows the extracted absorption coefficient of the unknown-nanocrystalline silicon layer on the substrate over the photon energy 1.4 to 5 eV. As shown in these results, the critical points Γ_1 and Γ_2, which correspond to the direct gaps of the energy band structure of material in the first Brillouin zone, seem to be slightly affected by the film thickness. Here, it is important to be pointed out that the Γ_1, Γ_2 critical points are released with the direct energy gaps at the first Brillouin zone of material while the L point corresponds to the indirect energy gap of material in the (111) direction. Thus, the absorption in this high energy regime reflects the total amount of Si-Si bonds, and is not affected by quantum confinement (QC) in z-direction. On the other hand, the indirect gap of the L point at the first Brillouin zone tunes with decreasing the film thickness (between 2 and 3.3 eV). However, in c-Si and poly-Si materials the oscillator strength corresponding to this indirect absorption peak has a very small value compared with the direct gaps of material at the center of Brillouin zone k = 0 [13]. The observation of indirect absorption peaks in our spectra results from an increase of the oscillator strength of the indirect transitions, due to the relaxation of the k selection rules via QC in z-direction. The enhancement of the oscillator strength of the indirect transitions has been estimated from PL data to be of the order of 10^4 [14].

It is interesting to note, that as shown from Fig. 2b the critical point of the indirect gap of the L point approaches that of the direct gap at the Γ_1 point for the smaller film thickness. This is attributed to the fact that in this NC size, the oscillator strength of the indirect gap in (111) direction has been increased considerably approaching the oscillator strength of the direct gaps of material. From this result, we may conclude that the QC effect in z-direction causes a significant enhancement of the oscillator strength. Furthermore, as extracted from our analysis the absorption coefficient in smaller NC sizes appears to have a significant reduction. This behavior was also previously reported [15] in Si-NCs embedded in SiO_2 matrix with sizes 4 nm and it was attributed to the shift of transition energies and the redistribution of the oscillator strength in this confinement regime.

3 Discussion Figure 2b shows the evolution of critical points in the first Brillouin zone for the direct and indirect gaps of nanocrystalline silicon films as a function of the film thickness. The direct gaps of material appear to have a small redshift 0.1 eV (black lines in Fig. 2b) with decreasing the film thickness. This behavior of the Γ point has been theoretically predicted for silicon with decreasing cluster size [16] but has not been observed experimentally. As shown in this figure, the L gap of material increases monotonically with decreasing the film thickness down to 5 nm as exactly predicted from the QC theory (green line in Fig. 2b) [17]. Furthermore, it is important to point out that for the sample with the film thickness of 25 nm we observe an additional interesting peak in the absorption spectrum at energy 2.85 eV (Fig. 2a). This peak depends on the vertical grain size since for the thicker sample (30 nm) it overlaps with the indirect gap of the L point (2.44 eV) whereas for the sample with thickness down to 10 nm it overlaps (3.35 eV) with the broad absorption peak of the Γ_1 direct gap. The extracted results for this peak are shown in Fig. 2b for all nanofilms. For the 5 nm thick film, the optical behavior seems to be very interesting. The two mentioned indirect gaps (green and red curves) appear to have a large band gap expansion (ΔE = 1.3 eV) compared with the bulk crystalline silicon value (star symbol at 2 eV). In order to give a more quantitative picture to our study, we should point out that the fitting curve throughout the experimentally extracted critical points (red line in Fig. 2b) has a parabolic dependence on the film thickness (or diameter of Si-NCs). This means that these critical points follow a characteristic behavior of the surface of the surrounding environment (probably oxygen-related bonds) [18] or grain boundary distortions [19].

4 Conclusions In concluding, we have investigated the dependence of the optical properties of very thin nanocrystalline silicon films on film thickness. We have found that the ellipsometric spectra of these nanofilms present a strong blueshift with decreasing the film thickness for both pseudodielectric functions. This is attributed to the vertical confinement of the samples in the growth direction (as depicted from TEM measurements) suggesting that the ellipsometric technique is a robust optical characterization technique for these nanofilms. These results could be extracted without any analysis of ellipsometric spectra. Furthermore, performing optical analysis of ellipsometric data and calculating the optical absorption coefficient, the direct gaps of material appear to have a redshift 0.1 eV as predicted from theoretical calculations, whereas the indirect gaps follow the QC theory. This is attributed to the enhancement of the oscillator strengths of indirect gaps compared with the direct gaps of material due to the redistribution of the k selection rules via QC in z-direction. The absorption in the high energy regime of direct gaps reflects the total amount of Si-Si bonds, and is not affected by QC in z-direction. In addition, an interesting critical point close related to the environment surrounding the core of NCs was observed. Fitting results of critical points as a function of the film thickness reveal that this absorption peak follows a quadratic behavior of the NC size and did not follow the QC model. With decreasing the film thickness down to 5 nm, QC effect in z-direction and surface-related states start to play a crucial role for the optical properties of these nanofilms.

Acknowledgements The authors would like to thank A. Antoniou from the University of Cyprus for the software assistance of two-layer structural model and Ch. B. Lioutas and N. Frangis from the Department of Physics, Aristotle University of Thessaloniki for performing TEM measurements. This work has been financially supported by the research programs EPYNE/0504/06 and EPYEΞ/0506/02 (NSILICON) funded by Cyprus Research Promotion Foundation.

References

[1] A. Salonidou, A. G. Nassiopoulou, A. Travlos, V. Ioannou-Sougleridis, and E. Tsoi, Nanotechnology **15**, 1233 (2004).
[2] M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, and A. J. Nozik, Nano Lett. **7**, 2506 (2007).
[3] A. G. Nassiopoulou and A. Salonidou, J. Nanosci. Nanotechnol. **7**, 1 (2007).
[4] E. Lioudakis, A. Othonos, A. G. Nassiopoulou, Ch. B. Lioutas, and N. Frangis, Appl. Phys. Lett. **90**, 191114 (2007).
[5] E. Lioudakis, A. G. Nassiopoulou, and A. Othonos, Appl. Phys. Lett. **90**, 171103 (2007).
[6] K. Tsunoda, S. Adachi, and M. Takahashi, J. Appl. Phys. **91**, 2936 (2002).
[7] E. Lioudakis, A. G. Nassiopoulou, and A. Othonos, Thin Solid Films **496**, 253 (2006).
[8] E. Lioudakis and A. Othonos, Opt. Eng. **44**(2), 023802 (2005).
[9] E. Lioudakis, A. Antoniou, A. Othonos, C. Christofides, A. G. Nassiopoulou, Ch. B. Lioutas, and N. Frangis, J. Appl. Phys. **102**, 083534 (2007).
[10] Ch. B. Lioutas, N. Vouroutzis, I. Tsiaoussis, N. Frangis, and A. G. Nassiopoulou, submitted to phys. stat. sol. (c) **5**(12), DOI 10.1002/pssc.200780224 (2008).
[11] M. Born and E. Wolf, Principles of Optics, 7th ed. (Cambridge University Press, 1999), p. 65.
[12] R. Azzam and N. Bashara, Ellipsometry and Polarized Light (North-Holland Publishing, 1977), p. 66.
[13] R. Hull, Properties of Crystalline Silicon (INSPEC, The Institution of Electrical Engineers, London, UK, 1999).
[14] M. Ben-Chorin, B. Averboukh, D. Kovalev, G. Polisski, and F. Koch, Phys. Rev. Lett. **77**, 763 (1996).
[15] E. Lioudakis, G. Hadjisavvas, P. C. Kelires, A. G. Nassiopoulou, and A. Othonos, Physica E **38**, 128 (2007).
[16] M. V. Rama Krishna and R. A. Friesner, J. Chem. Phys. **96**, 873 (1992).
[17] Klaus Sattler, The energy gap of clusters nanoparticles, and quantum dots, Handbook of Thin Films Materials, edited by H.S. Nalwa, Nanomaterials and Magnetic Thin Films, Vol. 5 (Academic Press, New York, 2002), p. 61.
[18] A.M. Ali, T. Inokuma, Y. Kurata, and S. Hasegawa, Mater. Sci. Eng. C **15**, 125 (2001).
[19] G. Hadjisavvas and P. C. Kelires, Phys. Rev. Lett. **93**, 226104 (2004).