

Structure of Si nano-clusters in ZnO matrix

J. García-Serrano^b, U. Pal

Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, México.

^bCentro de Investigaciones en Metalurgia y Materiales, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo Km. 4.5, Pachuca, Hgo. 42074, México.

The composite films of Si/ZnO were grown on quartz substrates by co-sputtering of Si and ZnO targets. Transmission electron microscope (TEM) images demonstrated a homogeneous distribution of clusters in the matrix with average size varied from 3.7 nm to 34 nm depending on the temperature of annealing. IR absorption measurements revealed the bands correspond to the modes of vibrations of Si₃ in its triangular geometrical structure, SiO_x and ZnO. By analysing the IR absorption and XPS spectra we could found that the nano-clusters consist of a Si₃ core and a SiO_x cap layer. With the increase of annealing temperature, the vibrational states of Si changed from the triplet ³B₁ (C_{2v}) and ³A₂ (D_{3h}) states to its singlet ground state ¹A₁ (C_{2v}) and the oxidation state of Si in SiO_x increased. The evolution of the IR bands with the variation of Si content in the films and with the variation of the temperature of annealing are discussed.

PACS: 61.46.+w, 78.66.-w, 78.30.-j

1. Introduction

The study of small atomic clusters has been the area of strong interest in recent years. Clusters of silicon atoms (Si_n) have received considerable attention both theoretically and experimentally. For instance, the diatomic cluster Si₂ has been well characterized spectroscopically [1]. In the case of the silicon trimer, the initial theoretical studies have been made by Grev and Shaefer [2] and Raghavachari [3]. Their results indicated that the Si₃ exhibits two quasi isoelectronic states (the ¹A₁(C_{2v}) and ³A₂(D_{3h}) state) and the singlet C_{2v} structure to be the ground state.

Experimentally, Weltner and McLeod [4] have measured the IR spectra of Si₃, obtained from the matrix isolation method and attributed to a linear chain structure. More recently, the infrared spectra of silicon clusters [5] produced by laser vaporization and trapped in rare gas matrices lead to the conclusion that the ¹A₁ state (C_{2v} symmetry) is the ground state of Si₃. The ¹A₁ (C_{2v}) state presents a triangular geometric structure with an apex angle of 80° and Si-Si bond length of 2.19 Å [2,3,5]. Many theoretical studies based on electronic structure calculations [2-4, 6-8] have predicted the relative stabilities of various Si_n isomers. However, the Si_n clusters has been detected only in vapor phase produced by different vaporization techniques [9-11].

We prepared Si nano-clusters in ZnO matrix on quartz glass substrates by r.f co-sputtering technique and carried out their IR absorption, XPS and TEM studies. In our previous work [12], we showed that the nano-clusters consist of a Si₃ phase surrounded by a SiO_x layer.

Our studies indicated that the Si in the clusters present a triangular geometry with both the apex angle and the bond length varying with the Si content and the annealing temperature of the films. In this paper, we focus on the studies of the structure of Si₃ clusters as a function of the annealing temperature and the variation of Si content of the composite films in details.

2. Experiment

Si/ZnO composite films were prepared on quartz glass substrates by co-sputtering of Si (5 X 5 X 0.3 mm³ wafers) and ZnO (100 mm diameter) targets with 100 W rf power at 10 mTorr Ar pressure.

The Si content in the films varied by changing the number of Si co-targets on the ZnO target. The films were annealed at different temperatures (400-800 °C) for 5 hours in vacuum (2 X 10⁻⁶ Torr). For the TEM observations, a JEOL JEM2000-FXII electron microscope was used. A Nicolet Magna 750 FTIR spectrometer was used to record the IR absorption spectra in diffuse mode.

The analysis of the shape of the IR absorption bands was carried out by the method of computer-simulated decomposition into Gaussian profiles.

3. Results and discussion

From the TEM micrographs we could observe the formation of homogeneously distributed nano-clusters in the matrix.

The average size of the clusters increased from 3.4 nm in the as-grown films to 34 nm for the films annealed at 800 °C. It has been observed that the increase of Si content in the composite films causes only an increase in the density of the clusters, without causing any significant change in their average size. Figure 1 shows two TEM images of the samples prepared with 12 Si co-targets and annealed at different temperatures.

Infrared absorption spectroscopy

In the frequency range between 400 and 580 cm⁻¹, the spectra of the composite films exhibit a broad non-symmetric band, the position and intensity of which change depending on their Si content and temperature of

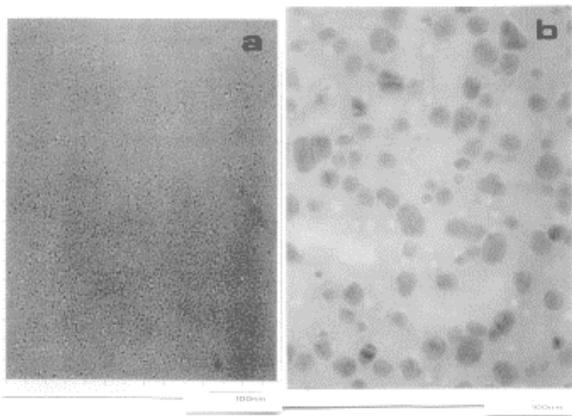


Figure 1. TEM images of Si/ZnO composite films prepared with 12 Si co-targets and annealed at (a) 400 °C and (b) 800 °C.

annealing. Figure 2, shows the dependence of the computer decomposed IR peaks on annealing temperature, for the films prepared with 16 Si co-targets.

The spectrum of the as-deposited film presents a peak at around 496 cm^{-1} , whereas, for the films annealed at 400 °C, an asymmetric band consisting two peaks centred at around 485 cm^{-1} and 512 cm^{-1} is seen. When the annealing temperature is increased to 600 °C, the spectrum showed an asymmetric band with two component peaks located at 508 cm^{-1} and 528 cm^{-1} . Finally, for the films annealed at 800 °C we observed a strong absorption band accompanied by a high frequency shoulder. The computer-simulated decomposition of the overlapped peaks revealed their positions at around 525 cm^{-1} and 552 cm^{-1} . Though, the absorption band of the films basically maintains two peaks in this frequency range, their position and the shape change with the variation of annealing temperature. The same effect is observed for all the samples.

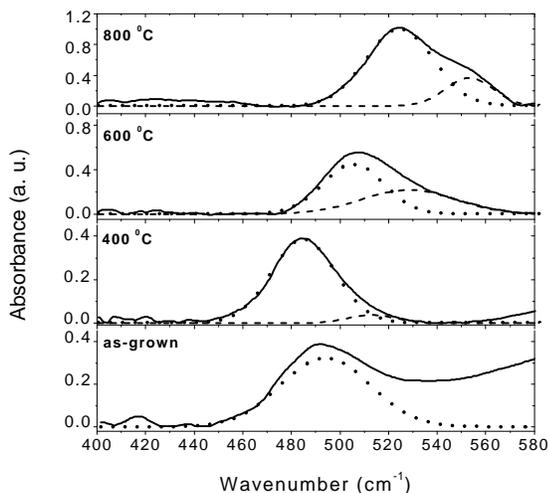


Figure 2. Dependence of IR spectra on annealing temperature for the samples prepared with 16 Si co-targets.

On the other hand, we observed two behaviors in the evolution of the IR absorption band when the Si content in the films is varied. First, in the films annealed at 700 °C or below, the absorption band shifted from higher frequencies to lower frequencies with the increase of Si content. Second behaviour is presented in the films annealed at 800 °C, where, the Si content increment did not cause any band shift; only the intensity of the absorption increased. In Figure 3, the evolution of the IR absorption peaks with the variation of Si content in the films annealed at 400 °C has been shown. The spectrum of the film prepared with 4 Si co-targets did not reveal any clear absorption band in this spectral range. In the spectrum of the film prepared with 8 Si co-targets, a peak centred at around 517 cm^{-1} is observed. However, as the number of Si co-targets increased to 12, the computer-simulated decomposition revealed two peaks located around 496 and 516 cm^{-1} . Both the component peaks moved towards shorter frequencies when the content of Si is increased further. The peaks moved from 496 to 485 cm^{-1} and from 516 to 512 cm^{-1} . With the increase of Si content, an increase of band intensity is clearly seen.

In Figure 4, the IR spectra for the films with different Si content and annealed at 800 °C are presented. We find that all the spectra exhibit two peaks centred approximately at 522 and 550 cm^{-1} . With the increase of the Si content, the position of these peaks did not change very much, however, the intensity of the two component peaks increased gradually.

Interpretation of IR absorption spectra

In order to interpret our spectra, we considered the previous experimental studies (Infrared spectroscopy [5], electronic absorption spectroscopy [11], photoelectronic spectroscopy [10] and zero-electron kinetic energy spectroscopy [9]) on the small silicon clusters and the *ab initio* calculations of electronic energies and vibrational frequencies in neutral Si_n ($n=2-8$) [2,3,8], with different geometrical structures.

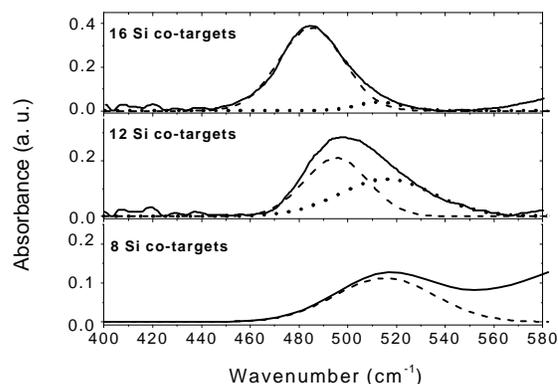


Figure 3. Evolution of the IR spectra with the variation of Si content for the samples annealed at 400 °C.

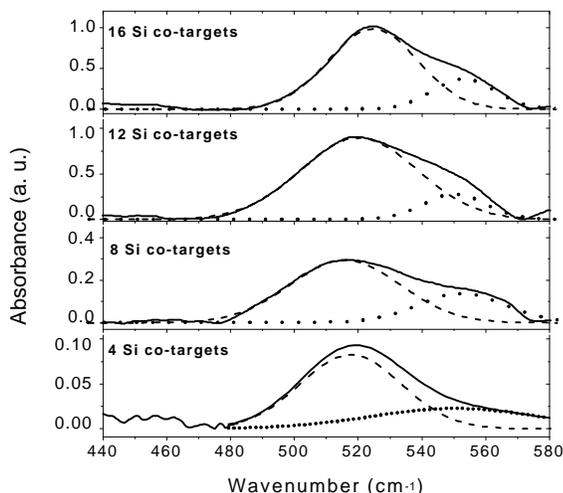


Figure 4. IR spectra of the samples with different Si content and annealed at 800 °C.

The results suggest that the absorption peaks observed in the IR spectra of our composite films originated, from the different vibrational modes of silicon trimer. The absorption peak at around 496 cm^{-1} in the IR spectrum of the as-grown film prepared with 16 Si co-targets (Figure 2) was tentatively assigned to the stretching symmetric (SS) vibrational mode of the Si-Si bond of the equilateral triangle structure (Figure 5-c) in its ${}^3A_2(D_{3h})$ excited state.

Our experimental peak position is very close to the calculated frequency ($501 \pm 10 \text{ cm}^{-1}$) [9]. The peaks centred at 485 and 512 cm^{-1} (for the film annealed at 400 °C) were assigned to the two different vibrational structures of Si_3 : The first peak (485 cm^{-1}) originated from the ${}^3B_1(C_{2v})$ excited state of the isosceles triangle geometry (figure 5-b), and is very close to the calculated frequency (481 cm^{-1}) reported by Rohlfiing and Raghavachari [13]. Whereas, the second absorption peak around 512 cm^{-1} correspond to the isosceles triangle structure of Si_3 (Figure 5-a) in its 4th most stable triplet state, which presents an apex angle of 123° [8]. The peaks located at around 508 and 528 cm^{-1} (for the films annealed at 600 °C) correspond to the SS vibrational mode of the equilateral triangle structure (Figure 5-c) in its ${}^3A_2(D_{3h})$ excited state and the asymmetric stretching (AS) vibrational mode of the isosceles triangle structure (Figure 5-d) in its ${}^1A_1(C_{2v})$ ground state respectively.

The isosceles triangle structure for the ${}^1A_1(C_{2v})$ ground state has an apex angle close to 80° and a Si-Si bond length of 2.190 Å [13]. Finally, we assigned the peaks observed at around 525 and 552 cm^{-1} (for the films annealed at 800 °C) to the AS and SS vibrational modes of Si-Si bond in Si_3 in its ${}^1A_1(C_{2v})$ ground state respectively. Our experimental peak positions agree perfectly with the values reported by S. Li et. al. [5].

By analysing our IR spectra of the samples with different Si content and annealed at 400 °C (Figure 3), we found that the component peaks correspond to three different geometrical structures of Si_3 : first, an isosceles triangle structure in its triplet state with apex angle of 123° (Figure 5-

a), generating the absorption peaks located at around 516 cm^{-1} (for the films with 8 Si co-targets) and 517 cm^{-1} (for the films with 12 Si co-targets). Second, the equilateral triangle structure (Figure 5-c) in its ${}^3A_2(D_{3h})$ state which originated the peaks at around 496 (for the films with 12 Si co-targets) and 508 cm^{-1} (for the films with 16 Si co-targets). Third, the isosceles triangle structure (Figure 5-b) in its ${}^3B_1(C_{2v})$ excited state, originating the peak at around 485 cm^{-1} (for the film with 16 Si co-targets).

As has been stated earlier, all the films prepared with different Si content and annealed at 800 °C revealed only two peaks at around 522 and 550 cm^{-1} (Figure 4). The interpretation of these IR spectra is rather simple, since we found that the peaks correspond only to one geometrical structure ${}^1A_1(C_{2v})$ (Figure 5-d), which is the most stable structure of the Si_3 . The vibrational frequencies of the Si-Si bond in ${}^1A_1(C_{2v})$ state are known experimentally to be close to 525 (AS) and 550 cm^{-1} (SS) [5].

So, the change of peak positions in our composite films is associated to the various geometrical structures of the Si clusters resulting from the variation of the Si-Si bond length and Si-Si-Si bond angle in Si_3 . By increasing the annealing temperature from 400 to 800 °C, the Si(atom 1)-Si(atom 2) bond length decreased for 2.333 to 2.190 Å.

4. Conclusion

In summery, we report the formation of Si nano-clusters in ZnO matrix by r.f co-sputtering technique. The effect of Si content and the annealing temperature on the variations of geometrical structure and vibrational states of Si_3 nano-clusters have been discussed. With the increase of Si content in the films, the Si_3 clusters

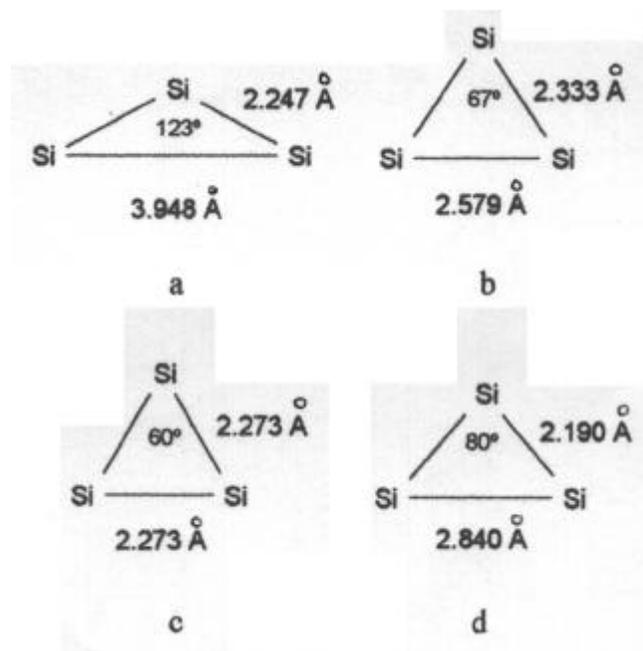


Figure 5. Possible geometrical structures assigned to Si_3 clusters as given by Fournier [8].

change from their more stable state to less stable state. Whereas, on increasing the annealing temperature, the clusters change from their less stable $^3B_1(C_{2v})$ state to more stable $^1A_1(C_{2v})$ state.

Acknowledgement

The work is partially supported by CONACyT, México (Project No. 28380E)

References

- [1] K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
- [2] R. S. Grev and H. F. Schaefer, *Chem. Phys. Lett.* **119**, 111 (1985).
- [3] K. Raghavachari, *J. Chem. Phys.* **83**, 3520 (1985).
- [4] W. Weltner and D. McLeod, *J. Chem. Phys.* **41**, 235 (1964).
- [5] S. Li, R. J. VanZee, W. Weltner Jr., K. J. Raghavachari, *Chem. Phys. Lett.* **243**, 275 (1995).
- [6] W. Andreoni, G. Pastore, *Phys. Rev B* **41**, 10243 (1990).
- [7] K. Raghavachari, C. M. Rohlfing, *J. Chem. Phys.* **94**, 3670 (1991).
- [8] R. Fournier, S. B. Sinnott, A. E. DePristo, *J. Chem Phys.* **97**, 4149 (1992).
- [9] C. C. Arnold, D. M. Neumark, *J. Chem. Phys.* **100**, 1797 (1994).
- [10] T. N. Kitsopoulos, C. J. Chick, A. Weaver, D. M. Neumark, *J. Chem. Phys.* **93**, 6108 (1990).
- [11] J. Fulara, P. Freivogel, M. Grutter, J. P. Maier, *J. Phys. Chem.* **100**, 18042 (1996).
- [12] U. Pal, J. García-Serrano, *Solid State Communications*, **111**, 427 (1999).
- [13] C. M. Rohlfing, K. Raghavachari, *J. Chem. Phys.* **96**, 2114 (1992).