Formation and vibrational structure of Si nano-clusters in ZnO matrix

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Recibido el 4 de mayo de 2000; aceptado el 19 de octubre de 2000

We have studied the formation and vibrational structure of Si nano-clusters in ZnO matrix prepared by radio-frequency (r.f.) co-sputtering, and characterized by Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and Infrared (IR) spectroscopy techniques. The composite films of Si/ZnO were grown on quartz substrates by co-sputtering of Si and ZnO targets. 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 Si_3 in its triangular geometrical structure. By analyzing the IR absorption and XPS spectra we found that the nano-clusters consist of a Si_3 core and a SiO_X cap layer. With the increase of annealing temperature, the vibrational states of Si changed from the triplet $^3B_1(C_{2\nu})$ and $^3A'_2(D_{3h})$ states to its singlet ground state $^1A_1(C_{2\nu})$ and the oxidation state of Si in SiO_X increased. The evolution of the local atomic structure of the Si nano-clusters with the variation of Si content in the films and with the variation of the temperature of annealing are discussed.

Keywords: Nanostructures; semiconductors; optical properties

Se estudia la formación y estructura vibracional de nano-cúmulos de Si en matriz de ZnO preparados por la técnica de radio-frecuencia (r.f.) co-sputtering, y caracterizados por Microscopía Electrónica de Transmisión (TEM), Espectroscopia Fotoelectrónica de rayos X (XPS) y Espectroscopia de Infrarrojo (IR). Las películas compósitas de Si/ZnO fueron crecidas sobre sustratos de cuarzo mediante el co-sputtering de blancos de Si y ZnO. Las imágenes de TEM mostraron una distribución homogénea de cúmulos en la matriz con un tamaño promedio de 3.7 nm a 34 nm dependiendo de la temperatura de tratamiento. Las mediciones de IR revelaron las bandas correspondientes a los modos de vibración de Si_3 en su estructura trigonal. Mediante el análisis de espectros de IR y XPS se encontró que los nano-cúmulos consisten de un núcleo de Si_3 rodeado por SiO_X. Con el incremento de la temperatura de tratamiento, se encontró que los estados vibracionales de Si cambian desde el estado triplete $^3B_1(C_{2\nu})$ y $^3A'_2(D_{3h})$ al estado basal singulete $^1A_1(C_{2\nu})$ y el estado de oxidación del Si en SiO_X aumenta. La evolución de la estructura atómica de los nano-cúmulos con la variación del contenido de Si en las películas y con la variación de la temperatura de tratamiento es discutida.

Descriptores: Nanostructuras; semiconductores; propiedades ópticas

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

1. Introduction

Interest in the synthesis, characterization, and understanding of materials with atomic dimensions has grown rapidly over the last decade owing to that these materials often exhibit properties that are quite distinct from those of the bulk material. Now, a large number of materials with nanometer size, such as thin films, multilayers, quantum dots, nanocomposites, nano-phase materials and atomic clusters on surfaces can be prepared. The study of small atomic clusters of semiconductor materials especially silicon, have received considerable attention both theoretically and experimentally in recent years. For instance, the diatomic cluster Si_2 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 Si_3 exhibits two quasi isoelectronic states (the $^1A_1(C_{2\nu})$ and $^3A'_2(D_{3h})$ state). Experimentally, Weltner and McLeod [4] have measured the infrared spectra of Si_3 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 $^1A_1$ state ($C_{2\nu}$ symmetry) is the ground state of Si_3. 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].

In the present work, formation and structure of Si nano-clusters in ZnO matrix were studied. Si nano-clusters in ZnO matrix were prepared on quartz glass substrates by r.f. co-sputtering technique and annealed subsequently at different

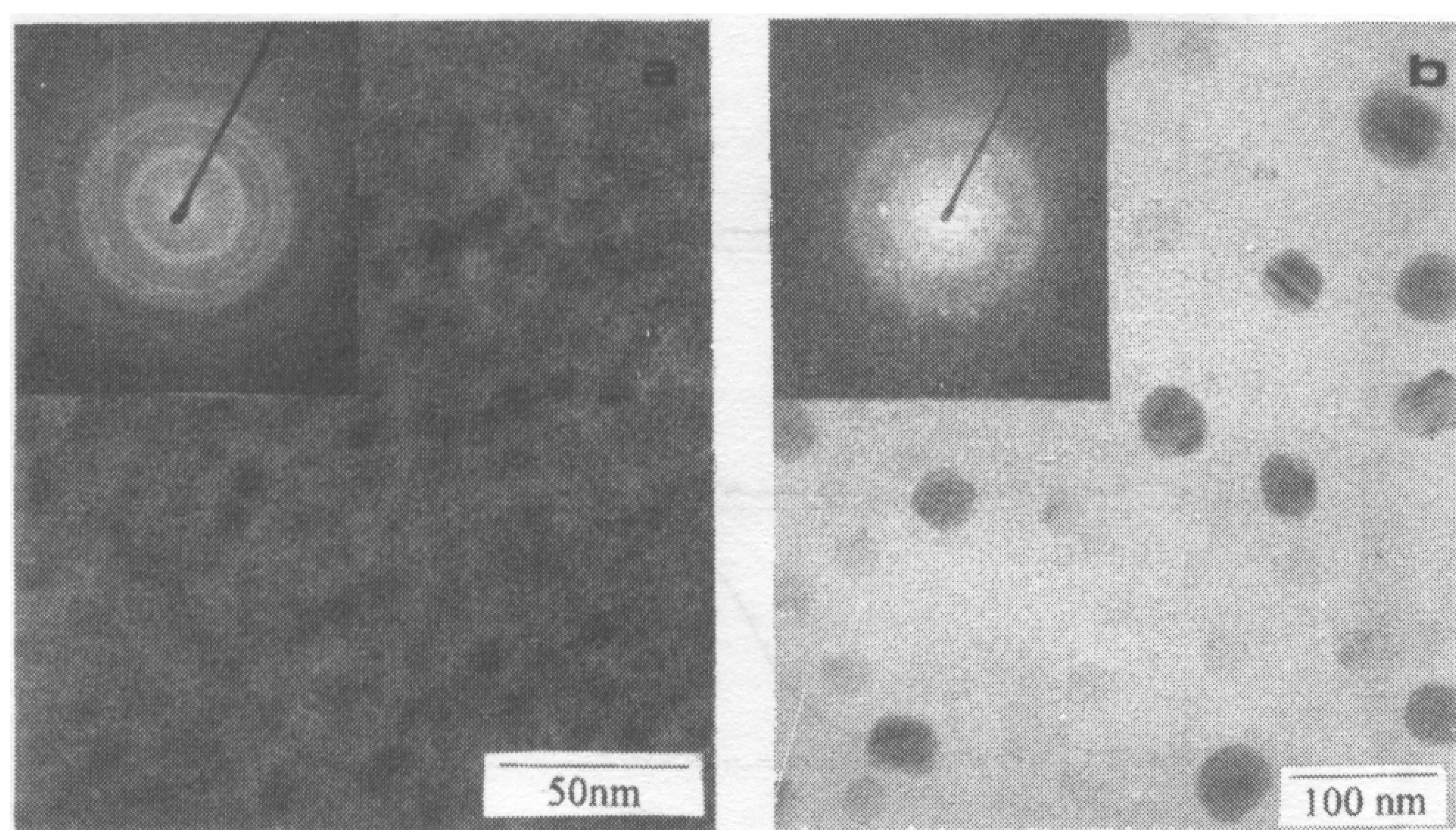


FIGURE 1. TEM and TED images of Si/ZnO composite films prepared with 12 Si co-targets (a) as-grown and (b) annealed at 800°C.

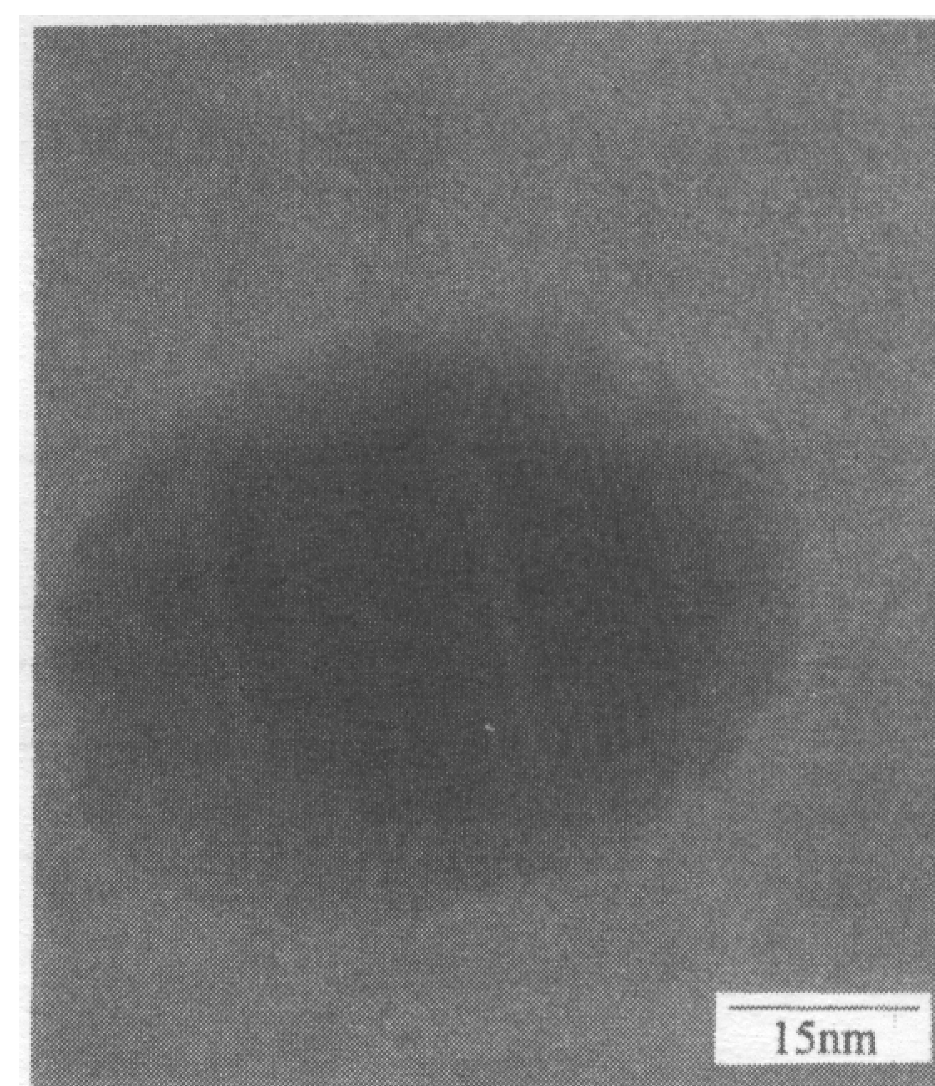


FIGURE 2. TEM and TED photographs of the crystallized clusters formed after annealing at 800°C.

temperatures. Their TEM, XPS and IR studies were carried out. Our studies indicate that the Si incorporated in the matrix, form nano-clusters, which consist of two layers; the core is constituted of Si_3 molecules and the cap layer is of SiO_X. We showed that the Si_3 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 samples. The oxidation state of Si in SiO_X increased with the increase of annealing temperature.

2. Experiment

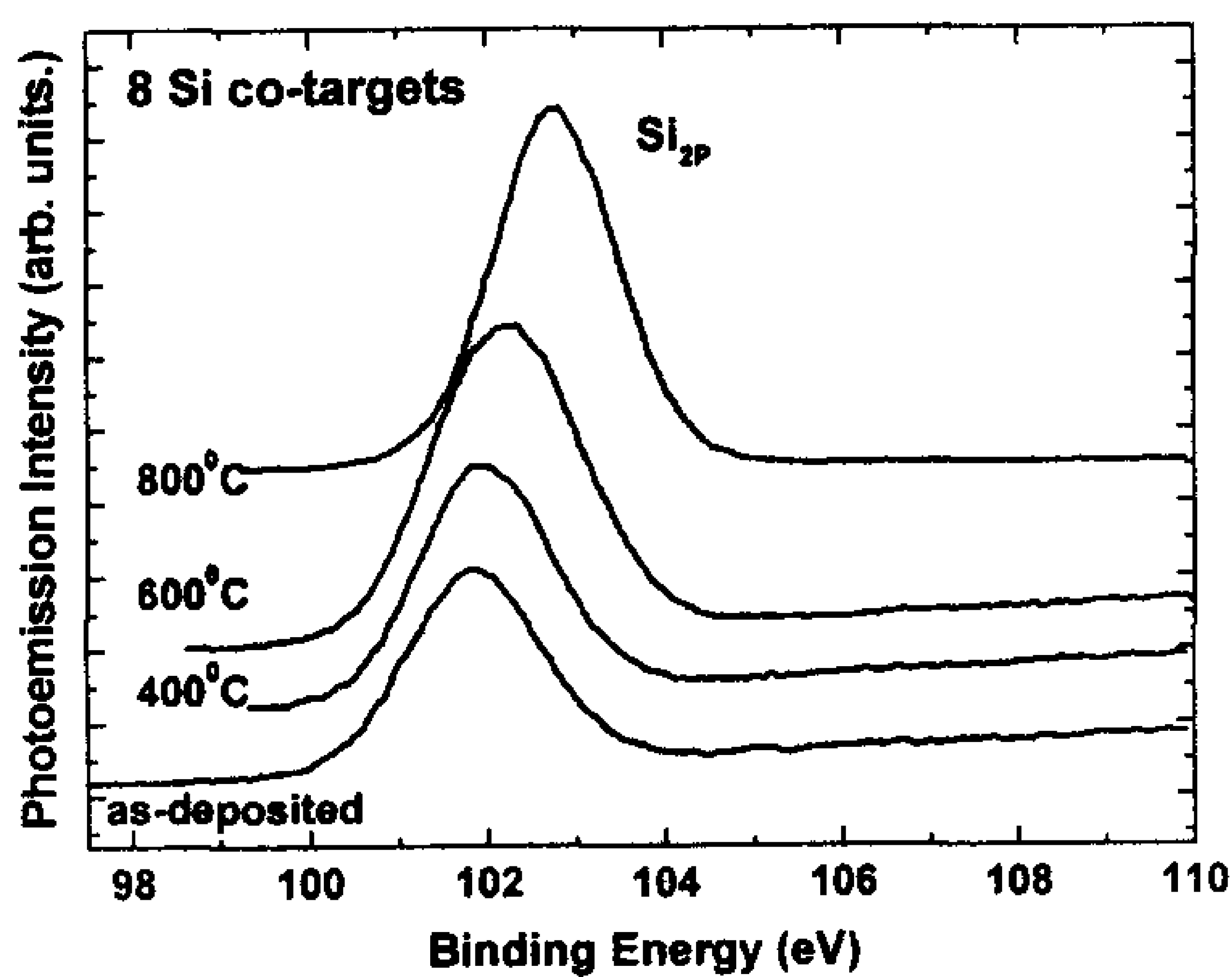
Si/ZnO composite films were prepared on quartz glass substrates by co-sputtering of Si ($5 \times 5 \times 0.3$ mm^3 wafers) and ZnO (100 mm diameter) targets with 100 W r.f power at 10 mTorr Ar pressure. The Si content in the films varied by changing the number of Si co-targets on the ZnO target, keeping the time of sputtering fixed (60 min). Depending upon the number of Si co-targets, the thickness of the films varied from 0.71 to 0.89 μm. The as-deposited films with different Si content were annealed at 400, 600 and 800°C for 5 hours in vacuum (2×10^{-6} Torr). The composition and chemical states of the elements in the films were studied by a Perkin-Elmer (PHI 5600ci) XPS system. 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

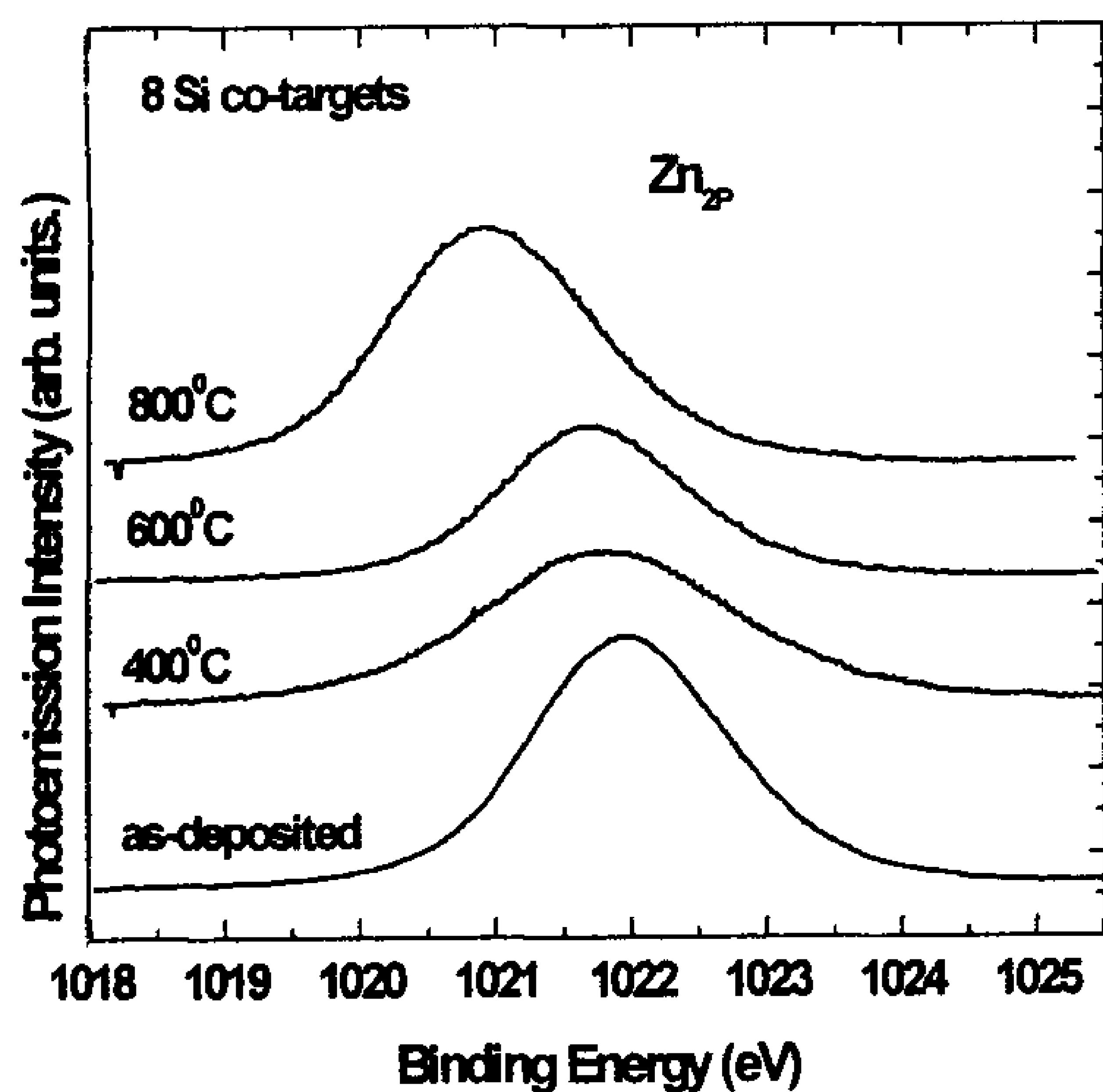
From the TEM micrographs we could observe the formation of homogeneously distributed nano-clusters in the matrix. In the as-deposited films, nano-clusters of average size of 3.4 nm were formed. When the annealing temperature is increased to 400°C and 600°C, the dimension of the nano-clusters did not increase noticeably. However, on annealing the films at 800°C, the nano-clusters aggregated to form bigger clusters, with an average size of 34 nm. 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 TEM images of the as-deposited sample prepared with 12 Si co-targets and after annealing at 800°C. The inserts show the corresponding TED patterns. In Fig. 2, TEM photograph of a typical crystallized cluster formed after annealing at 800°C is shown. It is interesting to notice that each cluster is composed of a crystalline core surrounded by an amorphous shell. The details of the geometrical structure of the clusters and their evolution on annealing and electron beam irradiation have been discussed elsewhere [12].

In Figs. 3a and 3b, typical examples of the evolution of the Si_{2p} and Zn_{2p} emission peaks in the XPS spectra with the variation of the annealing temperature are shown respectively. From the XPS spectra analysis of the Si/ZnO composite films, we could see that the position peak of Si remained in between the peak positions of elemental Si (99.2 eV) and SiO_2 (103.9 eV). The position of the Si_{2p} peak shifted from lower energy to higher energy with the increase of annealing temperature. This effect suggests that the Si particles in the clusters, undergo a thermal oxidation on heating of the samples, and remain in the SiO_X ($0 < X < 2$) chemical state. On the contrary, the energetic position of the Zn_{2p} emission peak (at approximately 1022 eV in as-deposited films) decrease monotonically with the progressive increase of the annealing temperature, approaching to the peak position of elemental Zn (1020.6 eV). It has been attributed to the breaking of Zn–O bonds caused by the increases of annealing temperature.

In the frequency range between 400 and 580 cm^{-1}, the IR spectra of the composite films exhibit a broad non-symmetric band, the position and intensity change depending on their Si content and annealing temperature. The band shifts towards higher frequencies with the increase of annealing temperature. Figure 4, shows the dependence of the IR band and its computer decomposed components on the variation annealing temperature, for the films prepared with 16 Si co-tar-



(a)



(b)

FIGURE 3. Evolution of the (a) Si_{2P} and (b) Zn_{2P} emission peaks with the variation of the annealing temperature.

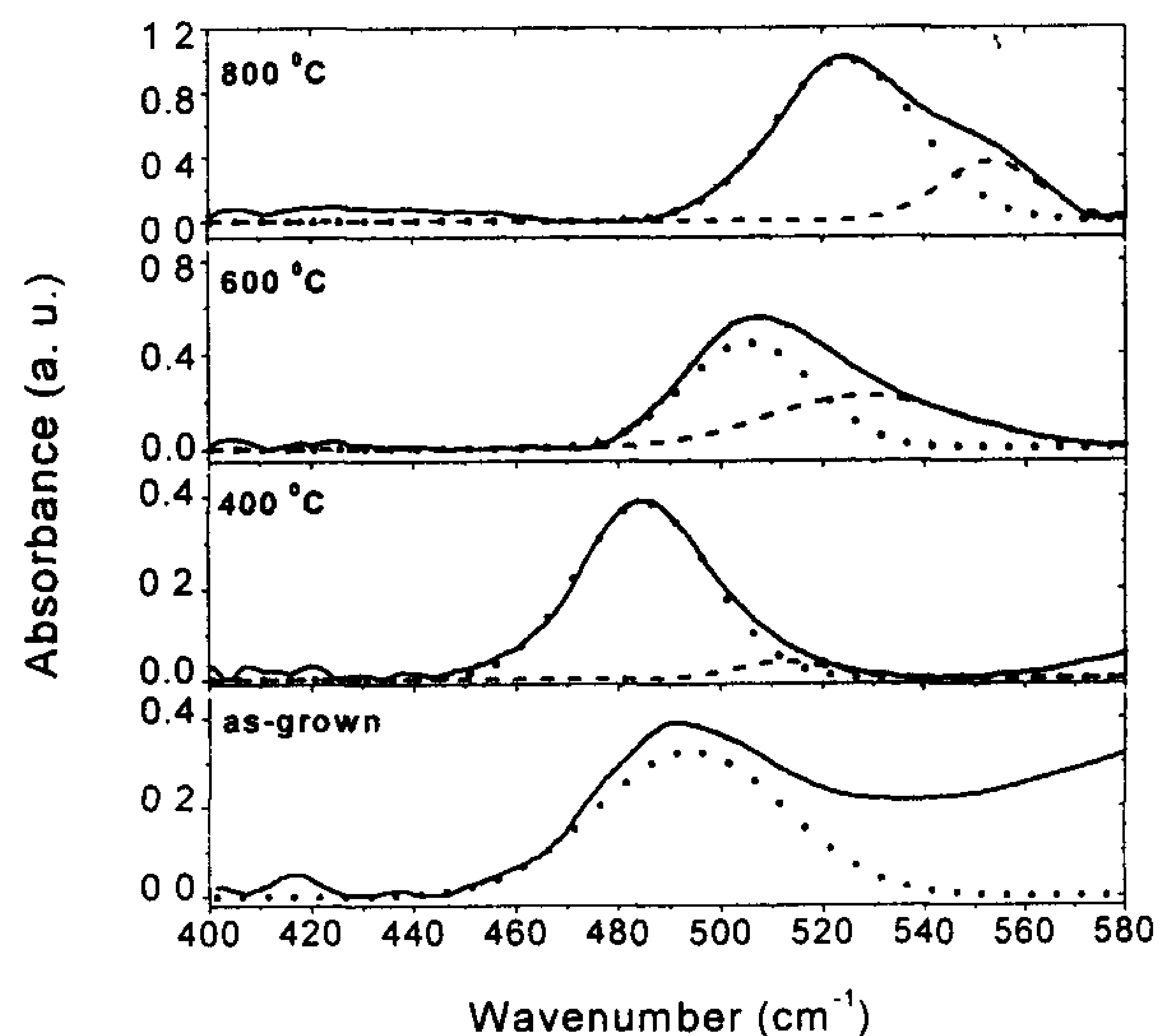


FIGURE 4. Dependence of IR spectra on annealing temperature for the samples prepared with 16 Si co-targets.

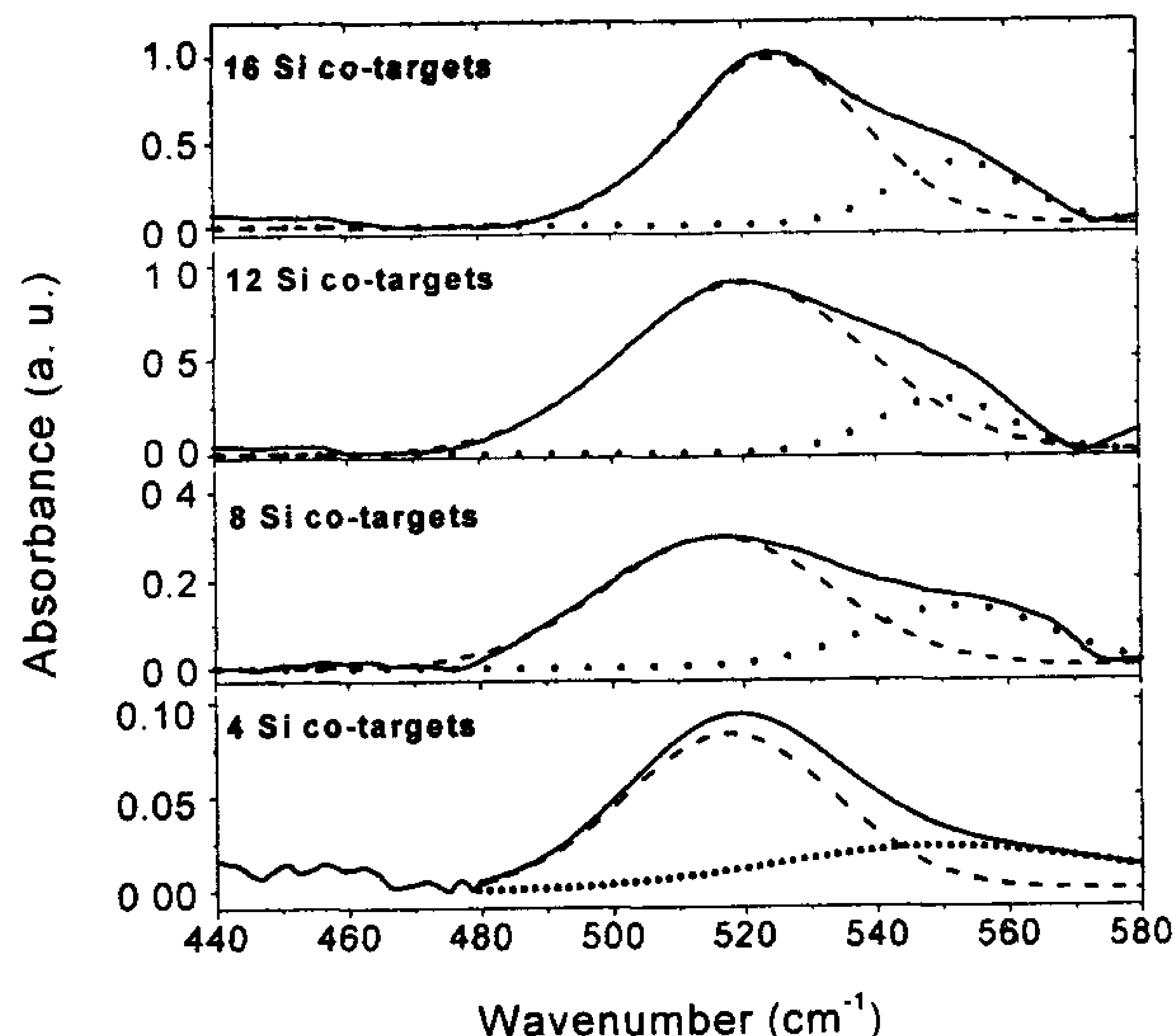


FIGURE 5. IR spectra of the samples with different Si content and annealed at 800°C.

gets. The spectrum of the as-deposited film presents apeak 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 revealed an asymmetric band with two peaks located at about 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 contains 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. In Fig. 5, 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 centered 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.

In order to interpret our IR 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 vibration frequencies in neutral Si_n (n =2–8) [2, 3, 8], with different geometrical structures. 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 (Fig. 4) was tentatively assigned to the stretching symmetric (SS) vibration mode of the Si-Si bond of the equilateral triangle structure (Fig. 6c) in its $^3A'_2$ (geometry D_{3h}) excited state. Our experimental peak position is very close to the calculated frequency (501 ± 10 cm^{-1}) [9]. The peaks centered at 485 and

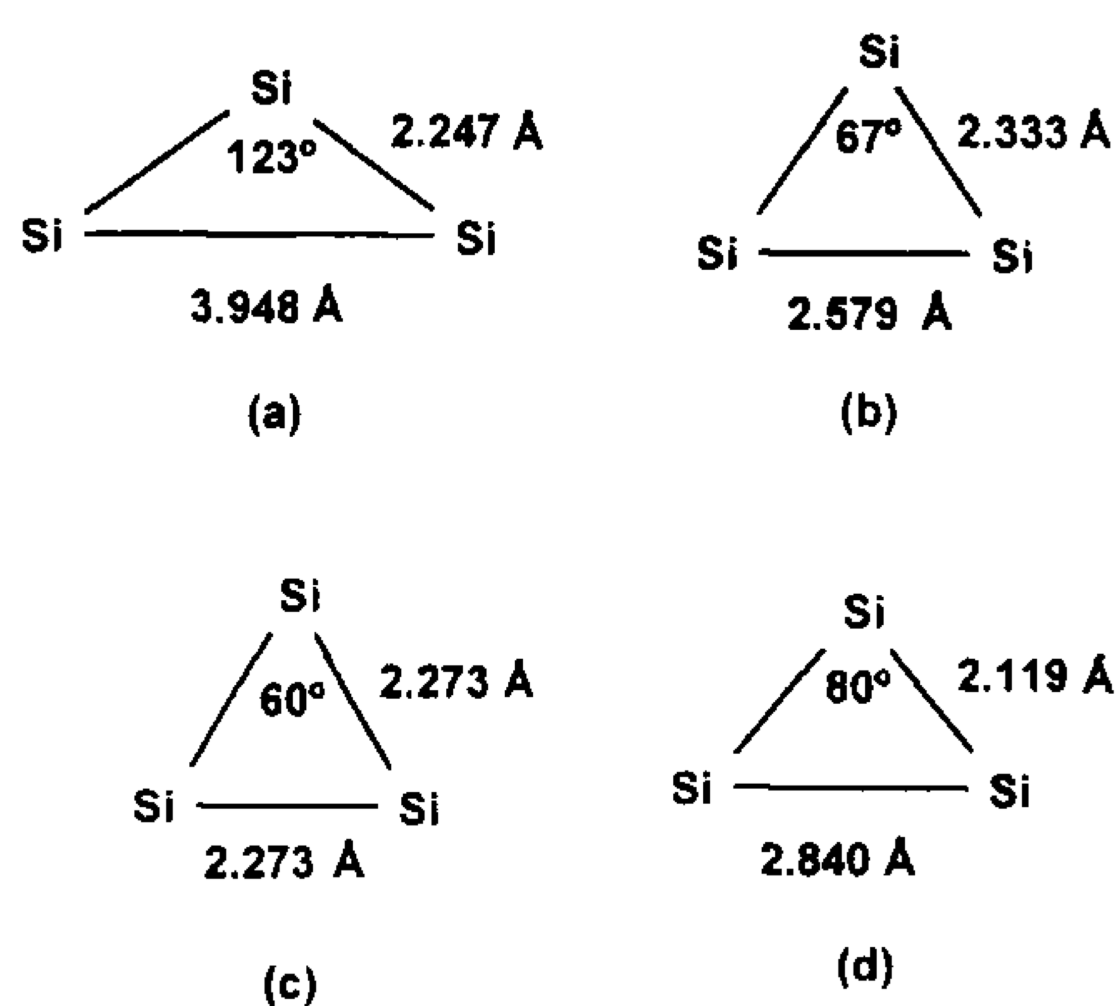


FIGURE 6 Possible geometrical structures assigned to Si_3 clusters as given by Fournier [8].

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 $^3B_1(C_{2\nu})$ excited state of the isosceles triangle geometry (Fig. 6b), and is very close to the calculated frequency (481 cm^{-1}) reported by Rohlfing and Raghavachari [13]. Whereas, the second absorption peak around 512 cm^{-1} corresponds to the isosceles triangle structure of Si_3 (Fig. 6a) 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 vibration mode of the equilateral triangle structure (Fig. 6c) in its $^3A'_2(D_{3h})$ excited state and the asymmetric stretching (AS) vibration mode of the isosceles triangle structure (Fig. 6d) in its $^1A_1(C_{2\nu})$ ground state respectively. The isosceles triangle structure for the $^1A_1(C_{2\nu})$ 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 vibration modes of Si–Si bond in Si_3 in its $^1A_1(C_{2\nu})$ ground state respectively. Our experimental peak positions agree well with the values reported by S. Li *et al.* [5]. 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} (Fig. 5). The interpretation of these IR spectra is rather simple, since we found that the peaks correspond only to one geometrical structure $^1A_1(C_{2\nu})$ (Fig. 6d), which is the most stable structure of the Si_3. The vibration frequencies of the Si–Si bond in $^1A_1(C_{2\nu})$ state are known experimentally to be close to 525 cm^{-1} (AS) and 550 cm^{-1} (SS) [5].

So, the change of peak positions in the IR spectra of our composite films is associated to the change of geometrical structure 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. Conclusions

In summary, we report the formation of Si nano-clusters in ZnO matrix by r.f co-sputtering technique. The size and chemical composition of these clusters are unique functions of the annealing temperature. The nano-clusters consist essentially of a Si_3 core covered with a coating of silicon oxide with different composition. 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 the annealing temperature, the clusters change from their less stable $^3B_1(C_{2\nu})$ state to more stable $^1A_1(C_{2\nu})$ state.

Acknowledgment

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

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