

Study on the optical absorption of oxygen-doped polysilicon thin films

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Abstract. Optical absorption measurements were used to study the optical properties of semi-insulating polycrystalline silicon (SIPOS) with different levels of oxygen dopings and a variety of annealing conditions. The optical properties of SIPOS were found to be closely related to the SIPOS microstructure. The absorption coefficient in SIPOS films with a high oxygen content displays a blue shift. From the absorption edge measurements, it has been observed that more band-tail states were introduced for the higher oxygen content samples. During the heat-annealing processes, changes occur in the absorption spectra of SIPOS: the absorption coefficient of SIPOS displays a blue shift, whereas after high-temperature ($T > 900^\circ\text{C}$) treatments, the absorption coefficient of SIPOS shows a red shift. These features of the optical properties of SIPOS are interpreted as the contribution of the distribution of Si-O bonds in the films and the recrystallization of SIPOS during low-temperature and high-temperature annealing processes, respectively.

Subject terms: optical absorption coefficient; oxygen-doped polysilicon; low-pressure chemical vapor deposition; annealing; oxygen content.

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1 Introduction

Semi-insulating polycrystalline silicon (SIPOS), as a new electronic material, has been used in a variety of electronic devices such as wide-gap emitters¹ for heterojunction transistors with high current gain and as excellent surface passivation films in semiconductor devices.^{2,3} As a new optoelectronic material, SIPOS has been applied to the highly efficient double heterojunction solar cells.⁴ Besides a continuously adjustable band gap, the refractive index of SIPOS films changes significantly with the oxygen content. These characteristics could be essential to optical device performance.

Although oxygen-doped polysilicon has recently been widely investigated,^{5–8} the optical absorption characteristic of SIPOS, deposited by low-pressure chemical vapor deposition (LPCVD), has not yet been reported. In this paper, we present the studies on the optical properties of LPCVD SIPOS with various oxygen contents and annealing processes through measurements of optical absorption to clarify the relation between the optical absorption and silicon phase structure and to explore the mechanism of optical absorption in SIPOS.

2 Experiments

2.1 Preparation of Samples

The SIPOS films were deposited by LPCVD at 650°C from $\text{SiH}_4 + \text{N}_2\text{O}$ on quartz substrates. The base pressure was

about 0.15 Pa and total chamber pressure during the deposition was approximately 106 to 133 Pa. The oxygen in the films, which was determined through infrared measurement, was varied from 8 to 36 at.%, controlled by the ratio of N_2O to SiH_4 gas flow in the reactor. The thickness d of the films measured 0.8 to 1.2 μm by a Talysurf profiler.

2.2 Optical Measurements

The absorption coefficient was determined from measurements of transmittance $T(\lambda)$, using a double-beam Perkin-Elmer 330 spectrophotometer. The absorption coefficient was calculated from the expression of Cody.⁹ In the low-absorption regime, where $\alpha d < 1$, the film's transmittance is

$$(T_{\max} \times T_{\min})^{1/2} = \frac{(1 - R_{32})(1 - R_{21}) \exp(-\alpha d)}{1 - R_{23}R_{21} \exp(-2\alpha d)} \quad (1)$$

In the high-absorption regime where $\alpha d > 1$, the film's transmittance is given by

$$T = |t_{12}|^2 |t_{23}|^2 n_3 \exp(-\alpha d) \quad (2)$$

$$r_{ij} = \frac{(n_i - n_j)}{(n_i + n_j)} \quad (3a)$$

$$t_{ij} = 1 - r_{ij} \quad (3b)$$

$$R_{ij} = r_{ij}^2 \quad i, j = 1, 2, 3, \quad (3c)$$

where r_{ij} and t_{ij} are the reflection and transmission coefficients; α is the absorption coefficient; d is the film thickness; n_1 , n_2 , and n_3 are the refractive index of the air ($n_1 = 1$), the thin film, and the substrate (for quartz $n_3 = 1.5$), respectively. Interference effects will appear when the wavelength of incident light approaches the film thickness. For

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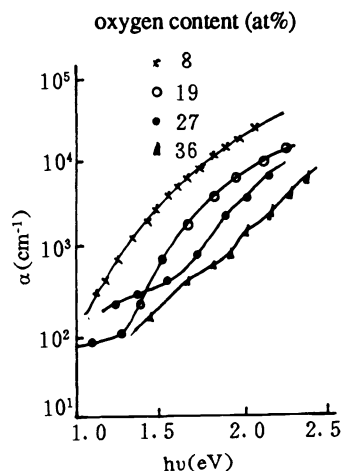


Fig. 1 Optical absorption versus photon energy for as-deposited SIPOS films of various oxygen contents.

shorter wavelengths, the increased absorption and the variations in the film thickness will damp the interference fringes and allow the use of Eq. (1) for the transmittance. For this measurement, the region of incident photon energy is in the 1.0 to 2.5 eV range. Also in this experiment, we used quartz substrates to minimize the substrate absorption and the effect of reflection between the substrate and the film.

3 Experimental Results

The optical absorption spectra of as-deposited SIPOS films with various oxygen contents are presented in Fig. 1. Figure 1 shows that optical absorption as a function of photon energy is divided into two regions: the curves are characterized by an exponential energy dependence at lower energies and a power law dependence (slowly varying shoulder) at higher energies. When the oxygen content is increased, the optical absorption spectra shift to high-energy power law behavior. Figure 1 also shows that high oxygen content samples even show a shoulder (power law dependence) at the lower energy region, that is, they appear to have an exponential *tail* effect associated with the neutral dangling bonds and the structural disorders in the films.

The optical absorption edge and optical gap (Tauc gap) E_{opt} with the oxygen content for as-deposited SIPOS films are shown in Figs. 2 and 3, respectively. The optical absorption edge of SIPOS films with high oxygen content shift to high energy (blue shift). Figure 3 shows that the relationship between E_{opt} and the oxygen content is approximately linear,

$$E_{opt} = 1.16 + 0.02(O) \text{ eV} \quad (4)$$

This feature is similar to that of hydrogenized amorphous silicon.

Annealing at different temperatures has modified the optical absorption of the films. Figure 4 shows the changes in the absorption coefficient with the annealing temperature T_a for SIPOS film with 8 at.% oxygen content.

1. When $T_a < 700^\circ\text{C}$, the spectra shift over to the high energy range, whereas in the low energy region the spectra is predominated by exponential dependence.

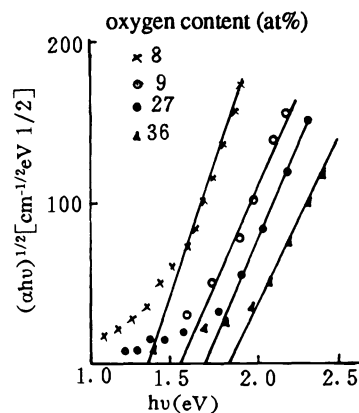


Fig. 2 Optical absorption edge versus photon energy for as-deposited SIPOS films of various oxygen contents.

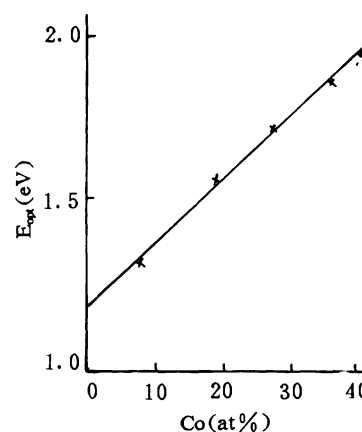


Fig. 3 Changes in the optical gap of SIPOS films as a function of oxygen content.

This feature implies that the tail effect is reduced with increasing T_a .

2. When $T_a = 700^\circ\text{C}$, the absorption spectra in the high energy region almost remain stable. But in the low energy region the film exhibits a shoulder in the optical absorption, i.e., the stronger tail effect appears.
3. When $T_a > 700^\circ\text{C}$, the spectra shift back to the low energy region and the exponential tail disappears. For comparison, in Fig. 5, we have plotted the E_{opt} as the function of T_a for the film (8 at.%). The E_{opt} monotonically increases when $T_a < 500^\circ\text{C}$ and rapidly decreases when $T_a > 700^\circ\text{C}$, while E_{opt} shows negligible changes when $500^\circ\text{C} < T_a < 700^\circ\text{C}$.

Figure 6 shows the optical absorption spectra of SIPOS films with various oxygen contents after annealing at 1100°C for 30 min. Comparing Fig. 6 with Fig. 1 shows that after high-temperature annealing the optical absorption spectra of all samples shift to the low energy range (i.e., display a red shift). In addition, the low energy part of absorption spectra presents an explicit exponential dependence. That is to say, the high-temperature annealing weakens the tail effect. But this weakening effect is less for the samples with a higher oxygen content.

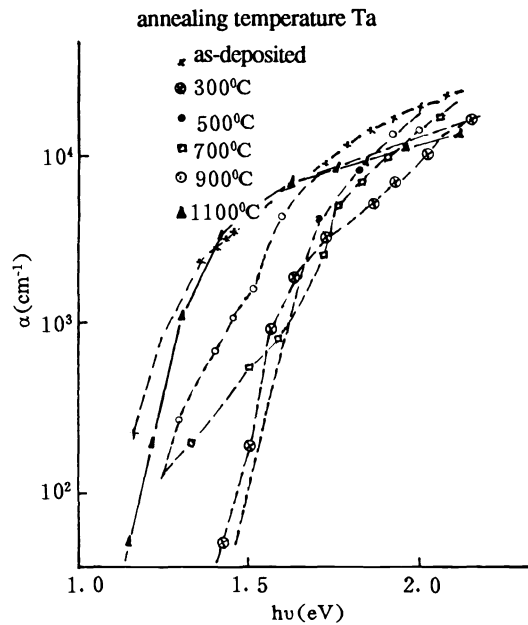


Fig. 4 Changes in optical absorption of SIPOS films (8 at.%) with annealing temperature T_a .

4 Discussion

Infrared analysis¹⁰ shows that the SIPOS films consist of at least two phases: pure silicon (Si) and silicon oxide (SiO_x). Oxygen atoms as interstitial impurities form Si-O bonds in the films while silicon atoms form Si-Si bonds. The optical absorption properties of SIPOS films must be related to the actions and distribution of Si-Si and Si-O bonds. At a higher oxygen content, the probability of Si-O bond formation is larger; whereas the probability of a Si-Si bond is smaller, resulting in a distribution of SiO_x . Because of the larger binding energy of a Si-O bond, increasing the oxygen content in SIPOS shifts the absorption spectra to a higher energy range, i.e., corresponding to a slight blue shift for α . Furthermore, for the higher oxygen content, the defects and disorders in film are greater, introducing more defect states in the energy gap. The optical transition between these localized states and extended states generates the tail effect in the low energy part of absorption spectra. Therefore, it is obvious that increasing the oxygen content induces much more tail effect.

From the experiment we found that the α of SIPOS films deposited by LPCVD is larger than that deposited by atmospheric-pressure chemical vapor deposition (APCVD).¹¹ The lower growth rates characteristic of the LPCVD system result in films containing a greater fraction of oxygen present in silicon-oxygen tetrahedral compared with more rapidly deposited APCVD films of similar content. The low growth rate allows oxygen atoms to diffuse laterally to the most energetically favorable site with a tendency towards complete oxygen coordination (i.e., forming Si-O-Si), resulting in more Si released from Si-O bonds to form Si-Si bonds and increasing the probability of forming Si-Si bonds in films with the same oxygen content. This feature makes SIPOS more similar to a-Si with larger α . This conclusion is in agreement with those of infrared analysis¹⁰ and Auger electronic spectrum analysis.¹²

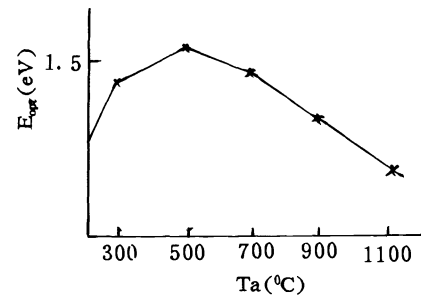


Fig. 5 Changes in the optical gap of SIPOS films with T_a .

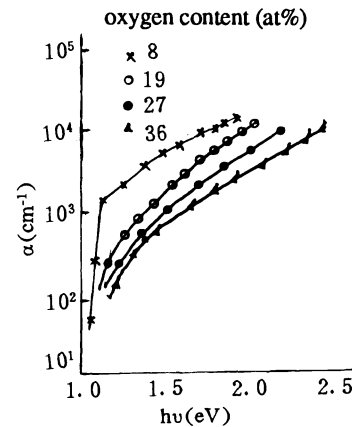


Fig. 6 Optical absorption versus photon energy for SIPOS films of various oxygen contents, after having been annealed at 1100°C for 30 min.

In the annealing processes, when T_a is not too high ($T_a < 700^\circ\text{C}$), some unbounded oxygen atoms form Si-O bonds from the dangling Si bonds because of thermal motion, thus increasing the numbers of Si-O bonds in the film and shifting the spectra to the high energy region, while decreasing the number of dangling Si bonds (i.e., some of the dangling Si passivated by oxygen atoms) and reducing the tail effect in the low energy part of the spectra. When T_a is about 700°C , oxygen atoms are released from Si-O bonds, resulting in the increase in dangling Si bonds and introducing more defect states in the energy gap, thus the low energy part of the spectra has a stronger tail effect. This agrees with our ESR measurement, where we found that the ESR spin density associated with the defects in the film has its maximum at $T_a = 700^\circ\text{C}$.¹³ When T_a is gradually raised ($T_a > 700^\circ\text{C}$), strengthening thermal motion, O atoms repulsed from the Si-Si network capture the Si-O bonds to form stable O-Si-O bonds. At the same time, because of high-temperature processing, the Si-Si network changes from disorder to order, nucleating Si grains in the network. In addition, Si atoms already bonded with the O atom in the network are released by thermal instability and then bind in the Si-Si network structure, while the O atom serves as an electronegative center to form a stable SiO_2 structure with Si-O bonds around the network. In this way, with higher T_a , the more stable Si-O-Si (SiO_2) are introduced in the film, whereas the Si grains grow because of recrystallization. So the high-temperature annealing process is a recrystallizing one, which makes the SIPOS films more or-

dered and moves the optical absorption spectra of films to the low energy range, i.e., a red shift. But for the higher oxygen content samples in the high-temperature annealing processes, as the increase in oxygen concentration suppresses the growth of Si grains in the films,¹⁴ the changes of spectra are less than that of lower oxygen content samples.

5 Conclusions

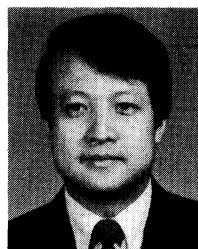
The optical absorption spectra of SIPOS films shift to the high energy range with an increase in oxygen content. There are two features of the optical absorption spectra that changes with T_a . When $T_a > 700^\circ\text{C}$, the film undergoes a recrystallizing process and the optical absorption spectra shift to the low energy range with less tail effect. When $T_a < 700^\circ\text{C}$, the absorption shifts to the high energy range, which is attributed to the redistribution of Si-O bonds in the film. At about $T_a = 700^\circ\text{C}$, a stronger tail effect occurs in the low energy part of the spectra, which results from the release of Si-O bonds in the film.

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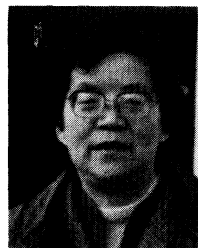
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