The Structure and Properties of Sn/SiSn-nanodisperse Alloy Thin Films

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Abstract. Near-infrared brain imaging technology has great advantages in brain imaging and inspection of brain disorders compared to traditional brain imaging technology. Silicon-tin (SiSn) alloys are expected to be the material for infrared brain imaging detectors. The structure and properties of the SiSn alloy thin films with relatively low Sn concentration, which are the key for it to be used in near-infrared brain imaging technology, have not been reported yet. Here, we report the deposition time, growth temperature, microstructure, resistivity, and transmittance of amorphous silicon-tin (a-Si₁₋ₓSnₓ) alloy thin films prepared by radio frequency (RF) magnetron sputtering. Reasonable deposition time and growth temperature for the preparation of the films are given in this paper. Sn nanocrystals are observed in the a-Si₁₋ₓSnₓ alloy thin films. The variations in resistivity and transmittance indicate that it has excellent electrical and optical properties so that it can be used as a near-infrared brain imaging detector material.

1. Introduction

Si remains a mainstream semiconductor material for numerous nanoelectronics, sensor and photovoltaic devices [1]. The alloying of Si with other IV group elements (SiGe [2], SiSn [3]-[5], SiGeSn [6]) is one way for apply Si to silicon-based devices because of their promising possibilities for band gap engineering and structural modification. Due to the diffusion process of tin (Sn) into the silicon lattice is low cost, scalable and manufacturable [7], the SiSn binary alloys are attracting considerable attention. At present, the preparation methods of SiSn alloy thin films mainly include co-evaporation technology [8], liquid phase epitaxy technology [9], ion beam induced epitaxial crystallization technology [10], chemical vapor deposition technology [11], magnetron sputtering [12] and molecular beam epitaxy [13]. The authors of [14] report the growth of epitaxial SiSn films with a Sn concentration from 10 to 35% and study the morphology and surface structure of the SiSn layers. The authors of [15] report the optical properties of such co-evaporated, nonhydrogenated amorphous silicon-tin (a-Si₁₋ₓSnₓ) alloys, with x varying from 0 to 0.5. In the paper describing of application of radio frequency (RF) sputtering to obtain SiSn films, it report the structural, electrical, and optical properties of rf-sputtered a-Si₁₋ₓSnₓ:H films in the composition range 0≤x≤0.51 [16]. The optical band gap of SiSn varies linearly with increasing Sn concentration, and many research efforts have focused on applying SiSn alloys to the mid-far infrared band by increasing the concentration of doped Sn. The near-infrared (NIR) region of 700-1700nm, due to its long tissue penetration depths and ultralow tissue backgrounds [17], [18], has great application value in NIR brain imaging. In this paper, we report the a-Si₁₋ₓSnₓ alloy thin films prepared by magnetron sputtering at relatively low concentration of Sn, and show that Sn is dispersed in a-Si₁₋ₓSnₓ alloy thin films in the form of nanocrystals. Further,
the microstructure, resistivity and transmittance of a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films, which is crucial for the NIR brain imaging, are studied in detail.

2. Experimental Procedure
The a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films were deposited onto Si wafers by co-sputtering. The starting materials were single crystal silicon (99.999% pure) and metallic tin (99.99% pure). The Si wafers were 1mm thick and were cleaved into 25mm × 15mm blocks to use as substrates for deposition. Sn concentration in the mixtures varied from 0% to 1%. The vacuum chamber is pumped down to a base pressure of 8.0×10⁻⁴ Pa. The chamber pressure was maintained at 4.3×10⁻¹ Pa after introduction of Ar (99.99% pure) with a flow rate of 75 sccm. For all films discussed in this paper, Si and Sn were deposited using an RF power of 200W. Substrate temperature varied from room temperature to 300°C and the time of deposition varied from 10 minutes to 30 minutes. The films that the Sn concentration is not given in this paper have a Sn concentration of 6%. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were employed to study the surface morphology of the films. The grain size of the films was characterized by X-ray diffraction (XRD). We also tested the transmission spectra and resistivity of the films to study its optical and electrical properties. Footnotes should be avoided whenever possible. If required they should be used only for brief notes that do not fit conveniently into the text.

3. Result and Discussion
To investigate the influence of deposition time on the film quality, a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films were deposited on Si substrates at a time range of 10-30min. Figure 1 presents the SEM images of the a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films prepared at room temperature for 10 min (a), 20 min (b) and 30 min (c). The surface of the films is irregular at a deposition time of 10 minutes as shown in figure 1 (a), and a large number of grains having a size of about several hundred nanometers appeared. We suspect that it should be metallic Sn, and the appearance of it is due to insufficient deposition time. As the growth temperature ascends to 20 minutes, as shown in figure 2 (a), the continuity of the films were improved, irregular grains on the surface of the films did not appear, but nanoparticles around 30nm appeared. According to the following XRD test, we can infer that the nanoparticles are Sn nanocrystals. As shown in figure 1 (c), the continuity of the films is better than that of 20 minutes when the deposition time increase to 30 minutes, and the number and size of Sn nanocrystals are decreased, indicating that 30 minutes is a reasonable deposition time.

![Figure 1](image_url)

Figure 1. SEM images of a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films at (a) 10min, (b) 20min, (c) 30min deposition time.

The growth temperature of the a-Si<sub>1-x</sub>Sn<sub>x</sub> alloy thin films also has a great influence on its quality. The effect of growth temperature on the microstructure and surface morphology of the films was also studied by SEM. The SEM images of the films grown at the different temperature are shown in figure 2. The surface morphology of the films prepared at room temperature, as shown in the figure 2 (a), is not ideal, and the size of Sn grains is not uniform. As shown in figure 2 (b), when the growth...
temperature reaches to 150℃, the size of Sn grains becomes smaller and the distribution of Sn grains is more uniform. The improvement is the result of high solubility of Sn in silicon at high temperature. When the growth temperature reached 200℃ and 250℃, the surface of the films as shown in figure 2 (c) (d) is more irregular than that prepared at room temperature. This is because during the deposition of the films, the silicon-tin binary alloy system will lower the melting point to about 200℃, and the temperature increases the solubility of Sn in silicon. However, when the deposition is completed, the solubility will start to decrease after cooling. Since the saturated solubility is reached before, as long as the temperature drops, the Sn will begin to precipitate a large amount of crystals, resulting in irregular film morphology.

Figure 2. SEM images of a-Si$_{1-x}$Sn$_x$ alloy thin films grown at (a) room temperature, (b) 150℃, (c) 200℃, (d) 250℃.

Figure 3 shows the XRD patterns of the a-Si$_{1-x}$Sn$_x$ alloy thin films with different Sn concentration. The samples with Sn concentration lower than 1% not show any characteristic diffraction peaks for crystalline Si or crystalline Sn. As the Sn concentration in the sample increases to more than 2%, many characteristic diffraction peaks of crystalline Sn were observed. With the increase of Sn concentration, the intensity of the characteristic peak increased, indicating that more Sn nanocrystals were produced in the samples. According to Debye-Scherrer [19], we calculated that the crystallite size of Sn in the Si$_{1-x}$Sn$_x$ alloy thin films is about 20-40nm, which is basically consistent with the results observed in the TEM images. The XRD patterns of the a-Si$_{1-x}$Sn$_x$ alloy thin films not show any characteristic peaks for crystalline Si, indicating the presence of amorphous Si.

Figure 4 shows the TEM images of the a-Si$_{1-x}$Sn$_x$ alloy thin films grown at room temperature and 150 ℃. The analysis by TEM is consistent with SEM and XRD results. It can be clearly seen in figure 4 that nanoparticles are present in the films, and it should be Sn nanocrystals by XRD pattern analysis. The size of Sn nanocrystals observed in figure 4 (a) is about 20-30nm, which is similar to that calculated by Debye-Scherrer formula. Compared with Sn nanocrystals in figure 4 (a), the number and
distribution of Sn nanocrystals in figure 4 (b) become smaller and more uniform separately. The size of Sn nanocrystals is also becoming smaller, which is consistent with the results of the SEM result.

Figure 3. XRD spectra of a-Si_{1-x}Sn_{x} alloy thin films for various values of x.

Figure 4. TEM images of a-Si_{1-x}Sn_{x} alloy thin films grown at (a) room temperature, (b) 150°C. The insets of (a) and (b) show the related diffraction pattern.

Excellent electrical property is a prerequisite for the application of SiSn materials to near-infrared brain imaging. Therefore, it is necessary to test its resistivity. As shown in figure 5, the resistivity of the a-Si_{1-x}Sn_{x} alloy thin films decrease about six orders when Sn concentration increases to 10%. Further, we also studied the effect of growth temperature on the resistivity of the a-Si_{1-x}Sn_{x} alloy thin films. Figure 6 shows the change in resistivity at different growth temperatures for the films with a Sn concentration of x = 0.10. Interestingly, in the temperature range of 100-150°C, the resistivity increases with the increase of temperature. As the growth temperature is further increased, the resistivity of the films begins to increase. We suspect that this change may be caused by competition between the following two mechanisms. On the one hand, the order of the a-Si_{1-x}Sn_{x} alloy thin films can be improved by increasing the growth temperature, and the increase in growth temperature promotes the formation of Sn nanocrystals, which reduces the dangling bonds of the lattice in the films.
These two points are the reasons for the decrease in resistivity of the a-Si$_{1-x}$Sn$_x$ alloy thin films. On the other hand, the increase of Sn nanocrystals consuming the Sn atoms in the Si lattice, resulting in a decrease in carrier concentration in the films, which eventually leads to an increase in resistivity.

![Figure 5](image5.png)  
**Figure 5.** Resistivity change at different growth temperatures.

![Figure 6](image6.png)  
**Figure 6.** Resistivity of a-Si$_{1-x}$Sn$_x$ alloy thin films.

In addition, we also studied the ratio of photo/dark conductivity variation of the a-Si$_{1-x}$Sn$_x$ alloy thin films caused by different Sn concentration. The ratio of photo/dark conductivity of the films first increases and then decreases as shown in figure 7. The reason for this is because when the concentration of Sn in the films is low, the Sn atoms replace the Si atoms in the a-Si lattice to increase the bright conductance of the films, resulting in an increase in the ratio of photo/dark conductivity. When the Sn concentration of the films increases to a relatively high value, the Sn atoms cannot replace the Si atoms in the a-Si lattice, thereby providing a large amount of free electrons, resulting in an increase in the dark conductivity of the a-Si$_{1-x}$Sn$_x$ alloy thin films.

![Figure 7](image7.png)  
**Figure 7.** Ratio of photo/dark conductivity of a-Si$_{1-x}$Sn$_x$ alloy thin films.

![Figure 8](image8.png)  
**Figure 8.** Transmittance spectra of a-Si$_{1-x}$Sn$_x$ alloy thin films for various values of x.

The transmission spectra of the a-Si$_{1-x}$Sn$_x$ alloy thin films were obtained by spectrophotometer. As shown in figure 8, the transmittance of the films in the visible wavelength region is very low, and tends to zero as the Sn concentration increases. The transmittance of the films in the near-infrared region decreases as the Sn concentration increases. The optical band gap of the films with different Sn concentration is shown in figure 9. The absorption wavelength corresponding to the optical band gap of the a-Si$_{1-x}$Sn$_x$ alloy thin films falls just in the near-infrared region, and the band gap decreases linearly with the increase of Sn concentration. The high absorbing rate will make SiSn become a promising material to be applied in near-infrared brain imaging detectors.
4. Conclusion
In this paper, the deposition time, growth temperature, microstructure, resistivity, and transmittance of the a-Si$_{1-x}$Sn$_x$ alloy thin films prepared by RF magnetron sputtering have been studied. The main conclusions of this work can be summarized as follows: (1) The reasonable deposition time and growth temperature for preparing the a-Si$_{1-x}$Sn$_x$ alloy thin films are 30 minutes and 150°C respectively. (2) Sn nanocatalysts are dispersed in the a-Si$_{1-x}$Sn$_x$ alloy thin films having a size of 20-30nm. (3) Significant resistivity reduction is obtained with the increase of Sn concentration and the ratio of photo/dark conductivity increases first and then further decreases with the increase of Sn concentration. (4) The transmittance of the a-Si$_{1-x}$Sn$_x$ alloy thin films decreases with increasing Sn concentration in both visible wavelength and near-infrared region, and the optical band gap decreases linearly with the increase of Sn concentration.

Acknowledgments
The authors thank to the National Natural Science Foundation of China (Grant no. 51372032).

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