Correlation between Band-gap and the Number of Defects in Titanium Silicide Thin Film

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Abstract: Ti-Si thin films for application in an infrared-ray sensor were manufactured using the rf-plasma CVD method. The growth mechanism which increased the internal diffusion of the titanium atoms was found to be associated with the reciprocal reaction of the dangling bonds generated by the desorption of hydrogen in the hydrogenated amorphous films. However, the morphology of the Ti-Si thin films became homogeneous with an increase in the annealing time. The grain boundary of the Ti-Si crystals was decomposed with the annealing of Ti/a-Si:H/Si(100) thin films fabricated by dilute gas (H₂). Titanium silicide exhibited a lattice structure of C54(311). In particular, the process showed a linear correlation between the number of defects and the band-gap. The ideal band-gap, which is possible to design the essential property, could be inferred from the linear relationship. Accordingly, it is possible to design the conditions for an optimum process to produce a specific number of defects in order to manufacture films with a specific band-gap.

Keywords: titanium silicide, band-gap, number of defects

Introduction

Among refractory metal silicides, titanium silicide is considered to be an optimal choice for application in an infrared-ray sensor because the material exhibits the lowest resistivity and a compatible band-gap. In a crystalline form, the adhesive property of TiSi₂ is admirable. As such, this material has been studied extensively as regards its reaction to high temperatures, physicochemical stability, resistance to oxygen, and compatibility with current fabrication processes [1-3].

Titanium silicide has a polymorph structure with thermodynamic stability. The two different crystal structures of TiSi₂ are C49 and C54 types. The C49 structure is base-centered orthorhombic, while the C54 structure is face-centered orthorhombic [4-6].

At a low temperature, the reaction starts with the formation of an amorphous silicide phase with an almost equi-atomic composition. The growth of this amorphous silicide has been found to be governed by a diffusion-controlled growth law. At slightly high temperatures (> 650°C), a crystalline disilicide phase has been observed [7].

When titanium silicide is fabricated within a range of ≤ 650°C, it forms amorphous thin films that show a high electric resistivity, because its mechanism exhibits the surface-diffusion of the rate-limited step. In contrast, when TiSi₂ is fabricated within a range of ≥ 650°C, it grows into crystalline thin films with a low electric resistivity. Typically, the C49 phase formation occurs at temperatures around 450 ~ 600°C, whereas the transition to the C54 phase occurs at temperatures greater than 650°C, and most previous studies have indicated that the C49 phase is stable between 500 and 600°C [8].

In order to manufacture TiSi₂ thin films with a pertinent band-gap, C49-TiSi₂ must be transformed into C54-TiSi₂. Titanium silicide formation is known to be affected by the impurity concentrations, Ti film thickness, and diffusion area etc [9]. As such it is assumed that both the growth rate and the transition temperature need to be controlled in the fabrication process.

In previous work, Titanium silicide has been fabricated by the physical deposition of amorphous Si and Ti at a low temperature using thermal treatment. However, the interface state is heterogeneous because the substrate is affected by the stress of heat. Thus, the quality of the resulting thin films is not suitable for an infrared-ray
sensor. Accordingly, in the present study, titanium silicide films were manufactured for a sensitive infrared-ray sensor within the range of near-IR. An infrared-ray sensor must be able to chase and discern an object for the slight temperature and light. Therefore, the fabricated films must show a band-gap of 0.3 eV to 1.6 eV. Thin films of hydrogenated amorphous silicon were deposited using rf-PCVD. 30 nm of metallic titanium was then physically deposited on the a-Si:H films using an e-beam evaporator under high vacuum conditions. The deposited films were annealed at a high temperature. The following issues were then investigated: the physicochemical and optical properties of the process parameters, phase determination, surface and lattice structure, and application. Potential in sensitive infrared-ray sensors based on the optical properties. In addition, the correlation between the band-gap and the number of defects in the fabricated films was examined in detail.

## Experimental

### Hydrogen Content

The hydrogen content in thin films influences their properties. Therefore, the transmittance and absorption coefficient were determined by a FT-IR analysis to appraise the effect of the hydrogen content in the hydrogenated amorphous thin films. The hydrogen content in the thin films was calculated using Equation (1) [10].

$$C_H[\text{\%}] = \frac{A_o [\text{cm}^{-2}] \cdot I_{540} [\text{cm}^{-1}] \times 100}{\rho_{Si-H} [\text{cm}^{3}]}$$

(1)

where $A_o$ is the oscillator strength [cm$^{-2}$], $I_{540}$ is the integrated absorption centered [cm$^{-1}$], and $\rho_{Si-H}$ is the density of the Si-H bond [g/cm$^3$].

### Number of Defects

The number of defects, $N_0$, was calculated using:

$$N_0 = \frac{1}{f_{oij}} \left( \frac{cmn}{2\pi^2e^2h} \right) \left[ \frac{3}{n^{2+2}} \right] \int a_{ex}(hn) d(hn)$$

$$= 8.21 \times 10^{18} \left[ \frac{1}{f_{oij}} \left( \frac{n}{n^{2+2}} \right) \right] \int a_{ex}(hn) d(hn)$$

$$= 1.586 \times 10^{14} \int a_{ex}(hn) d(hn)$$

where $c$ is the speed of light, $m$ is the electron mass, $n (=7.86)$ is the refractive index of TiSi$_2$, $e$ is the electron charge, $h \nu$ is the photon energy, and $f_{oij}$ is the atomic oscillator strength. Assuming $f_{oij} = 1$, a numerical prefactor of $1.586 \times 10^{14}$ was obtained [11].

### Experimental Procedure

The silicon wafers used were (100)-oriented, n-type, single-crystal Si wafers, phosphorus doped with a resistivity $\rho = 0.1 \sim 100$ cm. The organic material on the substrate was eliminated through treatment in a solution of $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 2$. After being rinsed in high purity water, the samples were etched in buffered HF : $\text{H}_2\text{O} = 1 : 30$, then blow dried with $\text{N}_2$ before being loading into an rf-plasma CVD reactor.

The hydrogenated amorphous silicon film was chemically deposited on the atomically clean Si substrates using the rf-plasma reactor. Then, the titanium films were deposited on the a-Si:H/Si (100) thin films by evaporation from a titanium filament using the vacuum coater. The base pressure in the chamber was $\approx 3.75 \times 10^{-3}$ Torr, and the deposition power was 200 watt.

The experiments were carried out to fabricate titanium silicide. The Ti/a-Si:H/Si (100) thin films were fabricated by dilute gas ($\text{H}_2$) and then were annealed at 700°C with $\text{N}_2$ ambient. The experimental conditions in the current study are summarized in Table 1.

The hydrogen contents in the films and the bonding state were calculated by a Fourier Transform-Infrared Spectrometer (FT-IR) analysis. The samples were also examined using Scanning Electron Microscopy (SEM) as regards the thickness and surface of the films. A X-ray Diffraction (XRD) analysis was carried out using a system for thin solid films, which kept an incident angle of CuKα source radiation and the range of the diffraction angle 2θ within 20–60°. Diffraction patterns were collected every second at room temperature. To examine the optical properties of the titanium silicide, the transmittance was determined within the range of near-IR.

### Results and Discussion

#### Annealing of Ti/a-Si:H/Si(100) Thin Films fabricated by Dilute Gas ($\text{H}_2$)

The deposition mechanism of a-Si:H using a dilute gas ($\text{H}_2$) has already been explained based on a vapor-phase
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![Graph showing film thickness and hydrogen content vs. substrate temperature](image)

**Figure 1.** Film thickness and hydrogen content of a-Si: H/Si (100) as a function of substrate temperature before annealing process.

The results on the thickness of the hydrogenated amorphous silicon thin films fabricated by dilute gas (H₂) and the hydrogen content are shown in Figure 1. In general, with an increasing substrate temperature, the Si-H bonds increased and the hydrogen atoms diffuse toward the outside of the films. This resulted from a reduction in the deposition rate. As the concentration gradient of the radicals and active species remained constant in the reactor, the hydrogen content was greatly dependent on the substrate temperature. With a low substrate temperature, the hydrogen contents in films became high and the defects were unable to bond to other molecules. Because hydrogen atoms do not desorb to the outside of the substrate, Si-H₃, and SiH₂SiH₃- ions and radicals exist on the ions of $\equiv$Si-Si:H₃ due to the surface reaction. Therefore, as the substrate temperature increased, the hydrogen content decreased due to the desorption of the hydrogen and decomposition of the dangling bonds, which act as a trap. The decrease in the hydrogen contents was caused by the desorption of the hydrogen due to the thermal-diffusion on the substrate surface.

![SEM images of titanium silicide prepared by Ti/a-Si:H/Si(100) at different annealing times](image)

**Figure 2.** SEM images of titanium silicide prepared by Ti/a-Si:H/Si(100) at different annealing times of (a) 6 hr and (b) 12 hr.
for 12 hr, along with the bonding of many grains.

However, as the annealing time approached 12 hr, continued thermal-diffusion occurred on the surface of the substrate. As a result, the films had a homogeneous morphology with almost the same size of grain.

Figure 3 shows the X-ray diffraction patterns of Ti/a-Si:H/Si (100) with annealing. The grown TiSi2 exhibited the sharp peak and lattice structure of C54 (311) at 2θ = 33°, both (a) and (b).

Figures 4 and 5 show the band-gap and number of defects under the same conditions as in Figure 3. The band-gap of the films suddenly decreased at 250°C when the substrate temperature was increased often 6 and 12 hr of annealing time. Yet, it only slightly increased at 300°C.

Fabricating the hydrogenated amorphous silicon, the dangling bonds formed due to the thermal diffusion on the surface of the substrate had an affect on the band-gap of the titanium silicide. The thermal diffusion was caused by the difference in the molecular weight and lattice structure. As a result, the mobility of the molecules was inconsistent. Accordingly, the best quality films with the
The slope exhibits the band-gap for the unit defect per unit volume [eV · cm$^{-3}$] and the intercept of the y-axis shows the ideal band-gap of the film with defects.

The ideal band-gap, which is the essential property, can be inferred from the linear relationship. Accordingly, the conditions of the process can be designed to produce a specific number of defects in order to manufacture films with a specific band-gap.

Therefore, the correlation between the band-gap and the number of defects was defined using the following model (Equation of Band-gap vs Number of Defects).

$$E_{g} = E_{N_{0}} + E_{N_{0}=0}$$

where, $E_{N_{0}=0}$ is the band-gap of an ideal thin film that is available to certificate lots of optical phenomena. The defects that act on the local level can be illustrated in the structure of the band-gap. In addition, the trapping phenomena that interrupt the transfer of the electron can also be understood.

**Conclusions**

Ti-Si thin films for application in an infrared-ray sensor were manufactured using the Ti/a-Si:H/Si(100) thin films. The Ti/a-Si:H/Si(100) thin films were fabricated by dilute gas ($H_{2}$) with a thermal annealing treatment.

As the annealing time of the Ti/a-Si:H/Si(100) thin films fabricated by dilute gas ($H_{2}$) increased, the grains were decomposed. For 6 and 12 hr of annealing time, the grown films showed a C54(311) epitaxial lattice structure. The band-gap was within the range of 0.5491–0.9627 eV, while the number of defects ranged from 0.0819–2.5235 × 10$^{18}$ cm$^{-3}$.

In particular, the process showed a linear correlation between the number of defects and the band-gap, and followed the expression of a model (Equation for band-gap vs number of defects).

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**References**