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Fabrication of $TiSi_2$ Using Microwave Hydrogen Plasma Annealing

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A new method, microwave hydrogen plasma annealing of sputter-deposited titanium films on an Si (111) substrate, was used to fabricate $TiSi_2$ films. The films were characterized by x-ray diffraction, Auger electron spectroscopy, sputter depth profiling, and four-point probe resistivity measurements. Polycrystalline $TiSi_2$, dominated by components with (040) orientation, was grown at the annealing temperature of 800 °C. The microwave hydrogen plasma was considered not only to provide the heat for the solid-phase reaction, but also to promote the solid-phase reaction by enhancing atom mobility and diffusion.

Keywords microwave hydrogen plasma annealing, silicide, titanium

1. Introduction

Metal silicide thin films are extensively used in the microelectronic industry as gate and local interconnects to reduce the series resistance of a device, as Schottky diodes in bipolar transistors to enlarge the switching speed, and as infrared (IR) image sensors. $TiSi_2$ is a silicide that is widely used in microelectronics applications, in part due to its favorable materials properties, including low electrical resistivity and high thermal stability.

Silicide can be formed by a solid-state reaction between metal and the Si bilayer, or by codepositing metal and Si, or by the chemical vapor deposition (CVD) of the silicide. To enhance silicide formation, many methods have been used, for instance, optimizing the target temperature with heating rates of 450 °C/s, ambient control, capping, ion beam mixing, preamorphization, introducing secondary impurities, and epitaxial growth (Ref 1). One of the key procedures used to form silicides is annealing, where rapid thermal annealing (RTA) is prevalent at present in the integrated circuit industries. Other annealing approaches include, for example, furnace annealing, Q-switched laser annealing, pulsed electron beam annealing (Ref 2, 3). The purpose of the present article is to describe a novel approach for forming $TiSi_2$ thin films using microwave hydrogen plasma annealing. Microwave annealing is a kind of rapid thermal processing approach that can raise the temperature of a sample at a rate of 200 °C/min compared with the 10 °C/min rate for conventional ceramic furnace annealing (Ref 4). It was brought forward that microwave hydrogen plasma annealing promotes atom diffusion in the solid-phase reaction between the thin Ti film and the Si substrate. Even though microwave annealing has been used to crystallize amorphous Si at low crystallization temperatures and short crystallization times with good film properties and anneal ceramic, this method has not been used to form silicides (Ref 5, 6).

2. Experimental

The wafers used in this work were p-type Si with a (111) orientation and the sheet resistivity of 17 Ω/cm. The substrates were cleaned according to the standard RCA process. Then the samples were rinsed in a dilute HF solution prior to being loaded into the ultra-high vacuum (UHV) magnetron sputtering system (ANELVA SPE-350). The ultimate vacuum in the sputtering system was $<10^{-3}$ Pa. The 100 nm thick Ti film and the 20 nm thick TiNi film were sputter-deposited on the Si substrate at room temperature without breaking the vacuum (argon pressure 3×10^{-1} Pa; power output 100 W). The TiNi film prevents the metal thin films from oxidizing during annealing. The sputtering rate for the Ti film was 20 nm/min.

The samples, about 2 × 2 cm on edge, were cut from the wafer and annealed in the hydrogen plasma that was generated by microwaves in a hermetically sealed quartz tube at 800 °C for 3 min. After the quartz tube was loaded with the sample and evacuated, the flow of hydrogen gas into the quartz tube was controlled via a flow meter and controller. The pressure in the quartz tube was kept at 2.5 kPa. The gradual increase in the power of the microwave generator caused plasma hydrogenation, forming the microwave hydrogen plasma around samples. The temperature can immediately increase and even reach >1000 °C; however, the preset annealing temperature was maintained by modulating the microwave power of the annealing system. During annealing, the sample temperature was measured by a two-tone IR pyrometer.

The sheet resistances of the silicide thin films were measured using a 4-point probe resistivity apparatus after microwave annealing. The silicide phases were identified by x-ray diffraction (XRD, Rigaku Dmax-rc). A scanning Auger microprobe (Microlab 310F) was used to obtain Auger electron spectroscopy (AES) spectra during sputter depth profiling of the sample.

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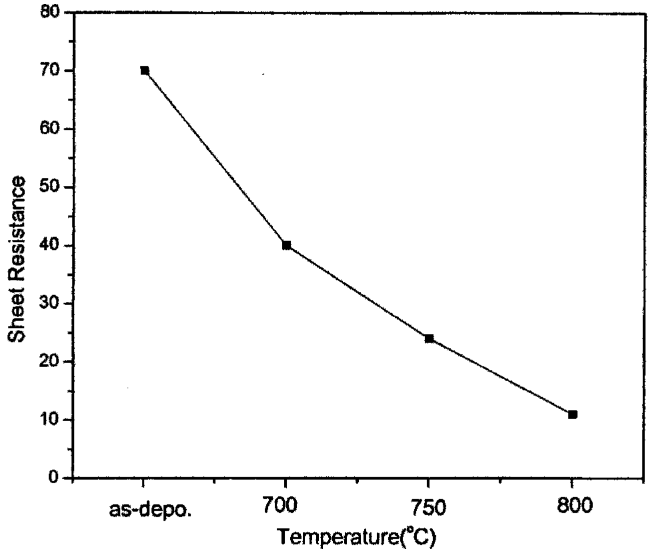

Fig. 1 Sheet-resistant transformation of 100 nm deposited Ti films after 3 min of microwave annealing at different temperatures

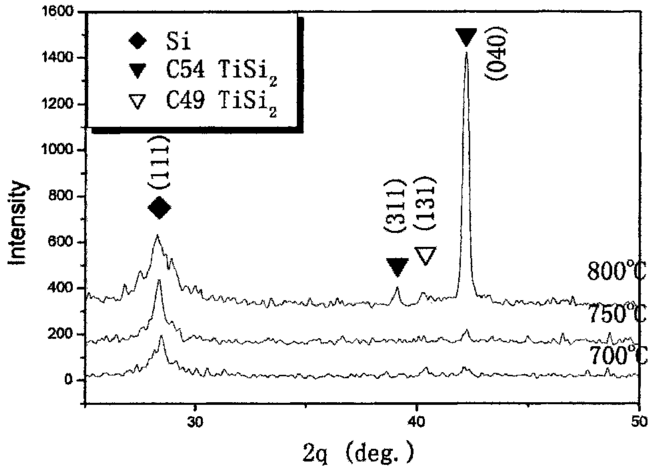

Fig. 2 The XRD spectra for 100 nm Ti films on the (111) Si after microwave annealing at different temperatures for 3 min

3. Results and Discussion

The silicide formation can be illustrated with the curves of sheet resistance versus annealing temperature and time. Figure 1 shows the sheet resistance of samples as a function of annealing temperature for 3 min of annealing. The sheet resistance decreased from 70 to 11 Ω/cm as the annealing temperature was increased. At 800 °C, the lowest sheet resistance was obtained. Specifically, the decrease in sheet resistance provides an indication of silicide formation.

The XRD spectra in Fig. 2 show that a small fraction of $TiSi_2$ formed when the annealing temperature was <750 °C. For $TiSi_2$, a dominant x-ray peak occurs at $2\partial = 42.2°$, with a weaker peak occurring at $2\partial = 39.1°$, corresponding to C54-$TiSi_2$ (040) and C54-$TiSi_2$ (311), respectively, could be measured after the samples were annealed at 800 °C. The peak of C54-$TiSi_2$ (040) is very pronounced when the sample was annealed at 800 °C. Hence, C54 $TiSi_2$ was formed between 750 and 800 °C in large quantities, supporting the nucleation-controlled mechanism (Ref 7). In Fig. 2, the Si peak from the (111) Si substrate was also clearly visible. The (040) structure is preferred in thin C54-$TiSi_2$ films (Ref 8).

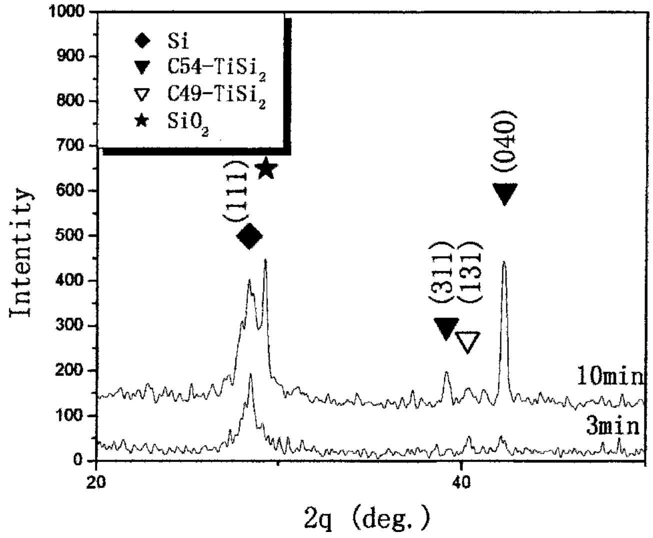

Fig. 3 The XRD spectra for 100 nm Ti films on the (111) Si after microwave annealing at 700 °C for 3 and 10 min

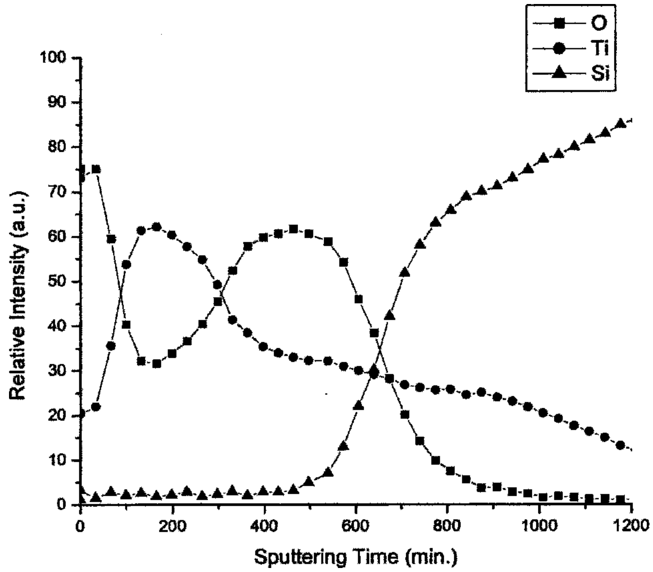

Fig. 4 The AES sputter depth profile of 100 nm Ti films on the (111) Si annealed at 800 °C

According to Fig. 3, only a small fraction of $TiSi_2$, either the C54 or C49 phase, formed when the sample was annealed at 700 °C for 3 min. The longer annealing time, 10 min, promoted significant growth of $TiSi_2$, because many prominent peaks were observed in the diffraction spectra, as shown in Fig. 3. The appearance of C54-type $TiSi_2$ at 700 °C showed that microwave hydrogen plasma annealing not only supplies the heat for a solid-phase reaction, but promotes atom diffusion between the Si and Ti bilayer as well. The enhanced mobility may be the result of the microwave alternating current field effect in which the electromagnetic field increases atomic mobility. Even though the microwaves are reflected by metal, it was considered that microwaves could indeed penetrate the nanometer thickness metal films and influence solid-phase reactions during microwave hydrogen plasma annealing.

To obtain a better understanding of atomic redistribution, analyses of Ti-Si films annealed at 800 °C for 3 min have been examined using AES, as shown in Fig. 4. After microwave hydrogen plasma annealing, it was evident that a solid-phase reaction had occurred at the Ti-Si interface, and Ti has reacted with Si to form $TiSi_2$. The AES also revealed the presence of oxygen atoms within the reacted Ti-Si film in Fig. 4. Because the native oxide formed at the Ti-Si interface before metal deposition, it was rather difficult to avoid oxygen contamination during $TiSi_2$ fabrication even under ultra-high vacuum conditions. Most of the oxygen migrated into the Ti layer all the way to the surface. However, the majority of the oxygen still resided below the surface. Hence, the Ti-Si interface is often equivalent to a Ti-Si-O ternary system, and the formation of SiO_2 coexisting with $TiSi_2$ has been reported (Ref 9, 10). Because the solubility of oxygen in $TiSi_2$ is lower than it is in the Ti layer, oxygen trapped in the Ti film is released and interdiffuses with the Si, forming SiO_2 at the $TiSi_2$ surface during annealing.

4. Conclusion

Microwave hydrogen plasma annealing has been used to fabricate $TiSi_2$ between Ti/Si (111), which demonstrates the feasibility to form Ti silicide using the new method. The $TiSi_2$ layer exhibits a dominant peak at (040) and a minor peak at (311) on the Si (111) substrate. 700 °C was the lowest temperature to form C54-phase $TiSi_2$ for 10 min annealing and the range between 750 and 800 °C was the formation temperature to grow C54-type $TiSi_2$ after 3 min annealing using the new method. More work should be done to explore the mechanism and the usage of using microwave hydrogen plasma annealing.

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