Effect of Silicon Surface Cleaning on the Initial Stage of Selective Titanium Silicide Chemical Vapor Deposition

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Selective titanium silicide Chemical Vapor Deposition (CVD) is a noteworthy method of forming self-aligned titanium silicide film on silicon surfaces to fabricate low resistant metal-silicon contacts in VLSIs. A number of studies on selective titanium silicide CVD have been reported, but the influence of Si surface cleanness on film growth has yet to be clarified.

We have found that the features and surface morphology of films are strongly influenced by the conditions of Si surfaces. This paper reports on the effects of Si surface cleaning on the Initial stage of film growth.

A cold-wall type reactor equipped with a heating room purged by Ar gas was used in this experiment. Si(100) wafers on which thermal oxide was formed and patterned were dipped in diluted HF, then dried and exposed to air. Native oxide on Si surface was deoxidized using 1-mTorr SiH₄ gas at wafer temperature of about 700°C. The end point of deoxidization was determined by observation of scattering laser light from the Si surface. The scatter is caused by Si nucleus growth with selective deposition. Titanium silicide was then selectively grown at the temperatures ranging from 700 to 740°C in a mixture of SiH₄ and TiCl₄ gases. The SiH₄ gas was supplied at a flow rate of 10 SCCM and at a partial pressure of 1 mTorr. The TiCl₄ gas was supplied at a partial pressure of 5-10x10⁻⁵ Torr. The film was analyzed using an x-ray diffractometer with a glancing x-ray angle of 2°.

Figures 1 and 2 show scanning electron microscope (SEM) photographs of the selectively grown titanium silicide with 2.5-h and 5-min exposure to air after the HF cleaning, respectively. Growth times of the titanium silicide are 8 min for Fig. 1 and 1 min for Fig. 2. The nucleus density shown in Fig. 2 is quite high in spite of shorter growth time. These results show that the nucleus density of titanium silicide is strongly influenced by surface cleanness.

Figure 3 shows a SEM photograph of the titanium silicide selectively grown after 5 min exposure to air and a native oxide deoxidization treatment using SiH₄ gas. A growth time in this case is 1 min. Since almost the entire Si surface is covered with small-grain silicide (200-500 Å), the film has a smooth morphology. The nucleus density with the deoxidization treatment is higher than that without the deoxidization.

Figure 4 shows x-ray diffraction pattern of titanium silicide grown for 2 min with the deoxidization treatment using SiH₄ gas. The peaks represent TiSi₂ formation. A 500-Å-thick titanium silicide film grown with the deoxidization treatment using SiH₄ gas has a low resistivity of about 15μΩ·cm.

In conclusion, it is clarified that the nucleus density of titanium silicide is greatly increased at the initial stage of film growth as the cleanliness of the Si surface is improved. Thin titanium silicide film with smooth morphology has been obtained by deoxidization of Si surface using SiH₄ gas prior to the titanium silicide growth.

(References)

Fig. 1. SEM photograph of titanium silicide grown after 2.5-h exposure to air after the HF cleaning.

Fig. 2. SEM photograph of titanium silicide grown after 5-min exposure to air after the HF cleaning.

Fig. 3. SEM photograph of titanium silicide grown after the deoxidization treatment using SiH₄ gas.

Fig. 4. X-ray diffraction pattern of titanium silicide grown with the deoxidization treatment.