Ohmic Contact in ECRCVD-TiN/Si Structure

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This is the first report that indicates CVD-TiN/Si ohmic characteristics. The contact resistance of TiN/Si structure that was formed by ECRCVD method using TiCl₄, N₂, H₂ and Ar gases has been investigated. Ohmic characteristics were obtained in both n⁺ and p⁺-Si contacts by only TiN film without a Ti layer under TiN film. The contact resistance depended on ECR plasma pre-treatment using Ar and H₂ gases just prior to TiN deposition and/or TiCl₄/N₂ gas introduction timing into the reactor. TiN/Si interface analysis indicates that this result was obtained by the removal of native oxide on Si with ECR plasma pre-treatment, and by suppression of the Si nitridation with gas molecular adsorption control on the Si surface.

I. Introduction

In the miniaturization of LSI's, the aspect ratio (defined by a ratio of depth to diameter) of contact/via holes has increased. Recently, because Low Pressure Chemical Vapor Deposition (LPCVD) method has better step coverage than the conventional sputtering method, blanket tungsten (W) CVD method has been applied to not only contact/via plug, but also interconnections 1). Titanium nitride (TiN) film is used as an adhesion layer for the blanket CVD-W film. It becomes difficult to obtain a good step coverage of TiN film in these holes by sputtering method. In order to solve this difficulty, CVD-TiN technology has been developed instead of sputtering 2-4). However, it is difficult to obtain sufficient electrical ohmic contact of TiN with Si particularly with p⁺-Si 5-6). Titanium (Ti) film has been interposed between the TiN film and Si to obtain the ohmic contact. However, the Ti film can not be deposited by usual thermal CVD. Recently, to obtain ohmic contact characteristics, collimate sputtered Ti film was reported to use as an underlayer of CVD-TiN film 7). However, this structure cannot be accepted from the basic concept of process development and economical point of view. Electron cyclotron resonance (ECR) CVD method using titanium tetrachloride (TiCl₄), hydrogen (H₂), nitrogen (N₂) and argon (Ar) gases, can deposit thick TiN films in the bottom of contact hole because of anisotropic growth. In this technology, Ti film can be also deposited by changing deposition condition 8).

In this paper, ECRCVD-TiN/Si ohmic characteristics were investigated, and it will be shown for the first time that the ohmic contact can be obtained even on p⁺-Si without a Ti intermediate layer.

II. Experimental

6 inch silicon (Si) (100) wafers were used in this study. After the field oxide was grown using a conventional LOCOS process, n⁺ and p⁺-Si diffusion layers were formed by implantation of As⁺ (40keV, 4E15cm⁻²) and BF₂⁺ (50keV, 4E15cm⁻²), and subsequent annealing at 900°C for 15 min. 2 μm of boro-phosphosilicate glass (BPSG) films were deposited and patterned to form contact holes of 0.5-1.0 μm in diameter on n⁺-Si and p⁺-Si layers. These samples were dipped in a diluted HF solution to remove native oxide on Si at contact hole bottom prior to loading into a CVD chamber. The 100 nm of TiN films were deposited on the samples with the ECR plasma CVD using TiCl₄, N₂, H₂ and Ar gases in a cold-wall, single wafer, LPCVD system equipped with a load-lock. The TiN deposition was carried out in the following steps. First, the wafer was heated at 420°C with a resistance heating. Second, ECR plasma was discharged using a gas mixture of Ar and H₂. We will abbreviate this to "ECR pre-treatment" here. The ECR plasma pre-treatment was done with the same microwave power of 2.8 kW at 420°C as the film deposition. Last, the TiN films were deposited by addition of TiCl₄ and N₂ gases to ECR pre-treatment atmosphere. The base pressure of the reactor was in the range of 2-3×10⁻⁶ torr. Deposition pressure was 1 mtorr. Because Ti film can be deposited using TiCl₄, H₂ and Ar without N₂ in this method, TiN/Ti (upper-layer/lower-layer) layers were also deposited successively in the same reactor on some samples. Thickness of the Ti and the TiN films were 0.50 nm and 100 nm, respectively. Then, all samples were annealed by rapid thermal annealing (RTA) at 760°C for 30 seconds in a N₂ ambient. For measuring the TiN/Si contact resistance, W plugs were formed by blanket W-CVD and etch-back, then TiN/AI/TiN layer as an interconnection was deposited by sputtering and patterned. The morphology of the interface between TiN and Si was observed by cross-sectional transmission electron microscopy (TEM). The crystal structure of the film at the interface was evaluated by microprobe electron beam diffraction. The crystal
The orientation of the TiN films with various deposition conditions was determined by X-ray diffraction (XRD).

III. Results and Discussion

Figure 1 shows the contact resistance of TiN/Ti structure on n* and p*-Si as a function of CVD-Ti thickness. The contact hole size and its aspect ratio are 0.5 μm in diameter and 4, respectively. As the Ti film thickness decreases, the contact resistance increases. In particular, this change with p*-Si is large. However, it should be noted here that even the TiN/p*-Si structure (Ti=0) shows about 600Ω of contact resistance. Figure 2 shows I-V characteristics of ECR-CVD-TiN/Si structure on both n* and p*-Si. Ohmic characteristics are obtained on both types of underlayers by the TiN film without a Ti underlayer.

The TiN/Si structure, in particular, the TiN/p*-Si structure, has been reported to show high contact resistance and almost nonohmic behavior. We found that ohmic contact was obtained using the ECR-CVD method in this experiment. In the ECR-CVD method, there are two major factors that affect TiN/Si interface. One is the ECR plasma pre-treatment using Ar and H2 just prior to the TiN film deposition. The other is that adsorption of deposition gas molecular on the Si surface can be controlled because TiCl4 gas can flow directly without a reaction with Si substrate at low deposition temperature. Therefore, our research was focused on ECR plasma pre-treatment time and introduction timing of TiCl4/N2 gases into the reactor. The dependence of the ECR-CVD-TiN/Si interface and that of contact resistance on the ECR plasma pre-treatment time and changing TiCl4/N2 gases introduction timing were evaluated. This pre-treatment time was changed from 5 seconds to 30 seconds. The change of the TiCl4/N2 gases introduction timing was done as follows. One was that N2 was made to flow earlier than TiCl4 by controlling gas valves. The delay time between N2 and TiCl4 was 4 seconds. The other was reverse sequence of that. The delay time between TiCl4 and N2 was 2.5 seconds.

The cross-sectional TEM micrographs of the ECR-CVD-TiN/Si interface formed by different conditions are shown in figure 3. Contact resistance of 0.8 Ωμm in diameter on n* and p*-Si in each case are also shown in the photographs. In sample (A), the TiN film was deposited on the Si substrate using the TiCl4/N2 gases introduction timing from TiCl4 to N2 after 5 seconds of the ECR plasma pre-treatment. In sample (B), the TiN film was deposited with the same gas introduction timing as the sample (A), after 30 seconds of the pre-treatment. In the case of sample (A), the contact resistance is higher than that of sample (B). The morphology at the interface between TiN and Si is very flat, in addition, thin amorphous TiN layer is observed. This layer was confirmed by microprobe electron diffraction. However, in the case of sample (B), the morphology at the interface is rough. Thin amorphous TiN layer was partially observed. The TiN film was directly grown on Si surface without the thin amorphous layer. It was reported that native oxide of Si was removed by ECR H2 plasma 5). It seems that the same reduction of native Si oxide occurs in the case of the ECR pre-treatment. Therefore, thin amorphous TiN layer was found to be deposited on the left native oxide on Si by insufficient ECR pre-treatment. This suggests the possibility that the left native oxide on Si increases the contact resistance between the TiN and Si, and suppresses direct growth of the TiN grain on Si. Thus, it is conjectured that the contact resistance depends on ECR plasma pre-treatment time using Ar and H2 gases.

On the other hand, in sample (C), the TiN film was deposited using the TiCl4/N2 gases introduction timing from N2 to TiCl4, after 30 seconds of the pre-treatment. Sample (C) has also the same flat morphology and thin amorphous TiN layer at the interface as the sample (A). Moreover, the contact resistance is very high. In this case, Si-N bonds were observed by XPS study at the Si surface by being exposed to ECR N2 plasma. Hence, the Si surface was found to be nitrided with ECR plasma discharge by earlier N2 gas introduction than TiCl4. Thin amorphous TiN layer was also found to be on the nitride of Si. Therefore, this result indicates that the nitridation of Si also increases the contact resistance between the TiN and Si, and suppresses direct growth of the TiN grain on Si. Accordingly, it is considered that adsorption of gas molecules on the Si surface affects the TiN/Si interface and the contact resistance.

Figure 4 shows X-ray diffraction patterns of these TiN/Si structure samples. ECR-CVD-TiN films preferentially have X-ray diffraction pattern oriented in the (200) direction. In the case of sample (B), peak intensity of TiN (200) is the strongest among three samples. Sample (A) and (C) had the weak peak intensity of TiN (200) because the thin amorphous TiN layer at interface, which was formed by native oxide and/or nitride of Si, seems to suppress the crystallographic continuity with Si (100) orientation. In other word, native oxide and/or nitride of Si that are formed by unsuitable pre-treatment and gas introduction timing, are found to suppress direct growth of TiN grains on the Si, and cause the high contact resistance with TiN/Si.

IV. Conclusion

Ohmic characteristics were obtained in both n* and p*-Si contacts by ECR-CVD-TiN film without a Ti underlayer for the first time. TiN/Si interface analysis indicates that this result was obtained by the removal of native oxide on Si with ECR plasma pre-treatment, and by suppression of Si nitridation with gas molecular adsorption control on the Si surface.

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References


Fig.3 Cross sectional TEM micrographs and contact resistance (0.8 μm²) of ECRCVD-TiN/Si structures

[(A) : ECR plasma pre-treatment 5sec,TiCl4→N2]
[(B) : ECR plasma pre-treatment 30sec,TiCl4→N2]
[(C) : ECR plasma pre-treatment 30sec, N2→TiCl4]

Fig.4 X-ray diffraction patterns of ECRCVD-TiN/Si structures

[(A) : ECR plasma pre-treatment 5sec,TiCl4→N2]
[(B) : ECR plasma pre-treatment 30sec,TiCl4→N2]
[(C) : ECR plasma pre-treatment 30sec, N2→TiCl4]