Suppression of Cu agglomeration in the Cu/Ta/Si structure by capping layer

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Abstract

Cu/Ta/Si (100) structures deposited by the non-mass separated ion beam deposition system showed a slight resistivity increase at 650 °C due to a Cu agglomeration. To suppress the Cu agglomeration on the Ta layer, a capping layer was deposited on the Cu/Ta/Si structure using Ta or SiO2 as a suppressor. In the case of the Ta suppressor, the agglomeration of Cu was observed between two distorted Ta films due to the difference in thermal expansion between the Cu film and the Ta film at high temperature. On the other hand, the SiO2 layer was found to be suitable as a suppressor, and the Cu agglomeration did not occur even after annealing at 650 °C by the suppression of the Cu diffusion.

Keywords: Ion beam deposition; Copper; Resistivity; Agglomeration

1. Introduction

Recently, Cu metallization has been extensively used for ultra-large scale integrated circuits because of its lower resistivity and superior electromigration resistance compared to Al alloy [1,2]. However, the interaction between Si and Cu is strong and detrimental to the electrical performance of the device even at temperatures below 200 °C [3]. For this reason, it is necessary to suppress the Cu diffusion into Si using an effective diffusion barrier. In our previous work [4], α-phase Ta diffusion barrier with a very low resistivity of about 40 μΩ cm was obtained by applying a substrate bias voltage of −125 V (hereafter: V5 = −125 V) using a non-mass separated ion beam deposition. Moreover, it was found that the thermal stability of the Ta diffusion barrier was mainly governed by the microstructure of the deposited layer.

In the case of the Cu/Ta/Si structures, a columnar structure of a Ta layer deposited at V5 = 0 V resulted in the lower failure temperature (300 °C) due to a Cu diffusion through Ta grain boundaries. On the other hand, when the negative substrate bias voltage of −125 V was applied, which means that Ta ions bombardment enhances the surface migration of Ta atoms on the substrate and results in the improvement of the film morphology, a Ta film without columnar grains showed a significant improvement in thermal stability up to 600 °C. The improvement of the failure temperature suggested that the advanced microstructure effectively played an important part in the suppression of the Cu diffusion. However, judging from the resistivity rise, the resistivity increase of the Cu/Ta (−125 V)/Si structure at 650 °C did not seem to be attributed to the diffusion of Cu through the Ta layer. Therefore, a further study is necessary to clarify the reason for the resistivity increase of the Cu/Ta (−125 V)/Si structure. In this work, the reason for the resistivity increase of the Cu/Ta (−125 V)/Si structure has been found to be due to a Cu agglomeration, and the suppression of the Cu agglomeration by capping layer will be examined.

2. Experimental

Fig. 1 shows a schematic diagram of the non-mass separated IBD system with RF sputter-type ion sources. The IBD apparatus consists of a deposition chamber and a load-lock system. A base pressure of 10−8 Pa is obtained in the deposition chamber using a turbo molecular pump. Two sets of ion sources, which are composed of RF (13.56 MHz) Cu coils and Cu or Ta sputter target, are located in the deposition chamber. The inner diameter of the RF Cu coils (five turns) is 57.5 mm. It is possible to deposit Ta and Cu
films on Si substrates continuously without exposing to the air. Rod shaped targets (Cu: 99.9999%, Ta: 99.99%) were electrolytically polished to eliminate the surface contamination, and then presputtered for 30 min to remove the surface contaminated layer prior to starting the deposition. Si (100) substrates with the dimension of 18 mm $\times$ 18 mm were ultrasonically cleaned in ethanol, etched by 5% HF solution, and then loaded on the substrate holder through the load-lock system. Substrate holders with the diameter of 50 mm were composed of commercial 99.99% copper.

Ar discharge plasma was generated at the RF power of 260 W. By applying a negative bias voltage ($V_T$) of $-300$ or $-500$ V to the Cu or Ta target, respectively, the Cu or Ta enriched plasma was generated. Since the copper coil was fully coated with Ta films due to an initial Ta plasma operation in the case of Ta films, an impurity contamination from the Cu coil could be prevented. Ta diffusion barriers (50 nm) were deposited on Si (100) substrates at $V_S = 0$ and $-125$ V. All Cu films (100 nm) were deposited at $V_S = -50$ V on the Ta/Si structures and Cu (100 nm)/Ta (50 nm)/Si structures were evaluated after thermal annealing up to 700 °C for 60 min in H$_2$ atmosphere. The value of $-50$ V has been found in our previous study [5] to be an optimum substrate bias voltage for preparing Cu films with a non-columnar structure, very low resistivity ($1.8 \pm 0.1 \mu\Omega$ cm), and smooth surface. The SiO$_2$ layer as a capping layer was deposited on the Cu/Ta/Si structure by RF magnetron sputtering with the RF power of 500 W under Ar atmosphere. A 99.99% SiO$_2$ target was used and the deposition rate was 4.38 nm/min. For the structural analysis of the films X-ray diffractometer (RIGAKU: RINT 2000) was used with Cu K$_\alpha$ radiation generated at 36 kV and 20 mA. The morphology of the samples was observed by FE-SEM (HITACHI: S-4100L), and the resistivity of the samples was carried out by the Van der Pauw method [6] using indium electrodes.

### 3. Results and discussion

As reported in the previous work [4], the failure temperatures of (a) the Cu/Ta (0 V)/Si and (b) the Cu/Ta ($-125$ V)/Si structures presented a remarkable difference as shown in Fig. 2. For the former structure, an abrupt rise of
the resistivity was observed at about 300 °C, suggesting that Cu has already reacted with Si substrate at temperature lower than 300 °C. The unexpected very low failure temperature of the Ta diffusion barrier deposited at $V_S = 0$ V seems to be due to the film microstructure consisting of small, clearly separated grains with noticeable cracks. On the other hand, the latter structure showed a considerable improvement in thermal stability up to 600 °C, and the resistivity increased until about 10 $\mu$Ω·cm at 650 °C. When the substrate bias voltage is applied, it leads to an increase in the kinetic energies of Ta$^+$ ions bombarding the surface. This high kinetic energy ion bombardment by an enhancement of adatom migrations results in decrease defect density and forming non-columnar structure. Therefore, this improvement of the failure temperature must be attributed to the microstructure without the columnar grains, suppressing the reaction of Si with Cu through Ta grain boundaries.

From SEM observations, it was found that Cu has been reacted with Si and formed Cu$_3$Si precipitates in the case of the Cu/Ta (0 V)/Si structure at 300 °C (not shown here), whereas in the case of the Cu/Ta (−125 V)/Si structure, island-like lumps on the surface of the Cu/Ta (−125 V)/Si structures were observed after the annealing at 650 °C as shown in Fig. 3. To reveal the nature of these lumps, this area was mapped using the X-ray energy analysis. Fig. 4 shows the SEM micrographs of the Cu (−50 V)/Ta (−125 V)/Si structure (a) and X-ray analysis map for Cu (b) and Ta (c). Ta is uniformly presented everywhere, whereas Cu signals converge on these lumps, which turned out to be agglomerated Cu. Accordingly, it was found that Cu atoms diffused at relatively lower temperature than its melting point and was agglomerated as shown in Fig. 3a. It was seen traces of Cu moved on the surface of the Ta diffusion barrier. It is also considered that the annealing at H$_2$ atmosphere promotes the agglomeration of Cu by the fast surface diffusion. From this result, the slight increase of the resistivity at 650 °C seems to be attributed to the starting of the Cu film agglomeration.

Considering the agglomeration of the Cu film, it is thought that the agglomeration seems to be related to the adhesion and/or wettability of the Cu film on the Ta diffusion barrier. Furthermore, Hara et al. [7] has recently...
reported that the stress of the Cu film itself on the barrier layer affects largely the agglomeration. The stress of the Cu films was determined quantitatively from the shift of X-ray diffraction spectra in Cu (111). The shift of the Cu (111) spectrum, $\Delta 2\theta$, can be given by [7]

$$\Delta 2\theta = 2 \tan \theta (\Delta d/d),$$  

(1)

where $d$ and $\Delta d$ are lattice constant and lattice distortion, respectively. Lattice distortion and the stress in the Cu film can be obtained from this equation, since the shift is proportional to the lattice distortion ratio ($\Delta d/d$). Therefore, if a big peak shift of Cu (111) peak in the as-deposited film could be observed by XRD analysis, it is certain that a high residual stress remains in the Cu film. It can reasonably be assumed that the residual stress of the Cu film enhances the agglomeration, because there is a peak observed in the as-deposited Cu film shifted by 0.3° to higher angle side. Therefore, it is considered that the agglomeration of the Cu film is a result of minimization of overall surface, interface and grain boundary energies by reducing the residual stress as well as the adhesion and/or the wettability of the Cu film [8]. In the thin film device fabrication, the agglomeration of Cu films would be a serious problem and an important factor for the formation of interconnecting wires with excellent resistance against electromigration [9]. Especially, the migration of Cu atoms by the surface diffusion could facilitate the agglomeration of the Cu film at high temperature. Then, if the surface diffusion of Cu atoms could be suppressed by capping layer, the failure temperature of the Cu/Ta ($\sim 125$ V)/Si structure could be expected to increase by the suppression of the Cu agglomeration.

At first, in order to suppress the Cu agglomeration on the surface, we tried to utilize Ta as a suppressor, which was deposited with about 150 nm thickness on the Cu/Ta ($\sim 125$ V)/Si structure at $V_S = -125$ V. The Ta ($\sim 125$ V)/Cu/Ta ($\sim 125$ V)/Si structure was annealed at 650 °C in H$_2$ atmosphere for 60 min. Surface and cross-sectional micrographs of the Ta/Cu/Ta/Si structure after the thermal annealing at 650 °C are shown in Fig. 5a and b. Unfortunately, the Cu film was agglomerated between two distorted Ta films. The upper Ta film rose largely on the surface, which seems to be caused by the difference in the thermal expansion between the Cu film and the Ta film [10].

Next, the SiO$_2$ was examined as another suppressor and 150 nm thickness SiO$_2$ was deposited by RF magnetron sputtering. The surface of the Cu/Ta ($\sim 125$ V)/Si sample was cleaned by presputtering before the deposition. Fig. 6 shows the cross-sectional micrographs of SiO$_2$/Cu/Ta/Si structure after the thermal annealing at (a) 650 °C and (b) 700 °C. The interface between the Cu film and the Ta barrier was not distinguished by the SEM observation. The agglomeration phenomenon was not found even after the annealing at 650 °C by the suppression of the Cu surface diffusion.

Fig. 7 shows the X-ray diffraction patterns of (a) the sample before and after annealing at various temperatures and (b) the enlarged scale at 700 °C. (110) $\alpha$-phase, (200) $\beta$-phase Ta peaks, and (111) strong texture of the Cu film were observed in as-deposited sample. No reactions involving Cu, Ta or Si were observed below 650 °C, although the intensities of the (111) Cu peak and (110) $\alpha$-Ta peak slightly decreased at 650 °C as shown in Fig. 7. This means that the Ta diffusion barrier deposited at $V_S = -125$ V could be stable up to 650 °C without a reaction of Cu and Si. For pure Ta diffusion barriers, since the failure temperature of the Ta layers was various ranging from 300 to 650 °C, it should be noted that the failure temperature of the Ta diffusion barrier deposited at $V_S = -125$ V using the non-mass separated ion beam deposition system is the highest one among the reported values. With further increase of the temperature up to 700 °C, however, spot-like precipitates occurred above the film surface in Fig. 6b, which suggests that Cu reacted with Si and formed Cu$_3$Si precipitates, and several new peaks were found and identified as TaSi$_2$ and Cu$_3$Si from XRD result as shown in Fig. 7b. In the present work, based on the above results, the Cu agglomerations could be suppressed by the SiO$_2$ capping layer, and then the failure temperature of the Ta diffusion barrier deposited at $V_S = -125$ V was found to be improved up to 650 °C. However, a further study for another capping layer like SiN to suppress the Cu
agglomeration will be required, since the SiO₂ layer is unsuitable to apply to the metallization technology in practice.

During the thermal annealing at high temperature, Cu atoms diffuse along the grain boundaries of the Ta layer into the Ta/Si interface where a nucleation of Cu₃Si takes place. After an initial stage of the nucleation, the Cu₃Si phase grows during the annealing at high temperature [11], which leads to the formation of the observed large Cu₃Si precipitates. Laurila et al. [12] have also observed the Cu₃Si precipitates in the Cu (400 nm)/Ta (100 nm)/Si structures annealed at 685 °C. Furthermore, because the Cu₃Si precipitates are associated with a large volume expansion of 150%, the Cu₃Si precipitates, as shown in Fig. 6b, are considered to rise above the film surface after the volume expansion. Since the reaction between Ta and Si requires quite high temperatures (above 650 °C), it is not surprising that Ta reacted with Si forms TaSi₂ at 700 °C as indicated in Fig. 7b. The nucleation and growth of a Cu₃Si probably introduces a driving force of the TaSi₂ formation at the Ta/Si interface because the Cu₃Si phase initially nucleates at the Ta/Si interface. According to Laurila et al. the formation rate of TaSi₂ is mainly governed by the release rate of Si atoms from the Si lattice. Therefore, it is highly possible that the formation of Cu₃Si by Cu diffusion through the Ta layer helps to release the Si atoms and enhance the formation of TaSi₂ at high temperature.

4. Conclusions

Cu/Ta/Si (100) structures were fabricated using the non-mass separated IBD system. It was found that the reason for a slight resistivity increase of the Cu/Ta/Si structure at 650 °C was due to a Cu agglomeration without Cu diffusion through the Ta layer. The suppression of the Cu agglomeration on Ta barrier layer by capping layer was evaluated using Ta and SiO₂ as a suppressor. In the case of the Ta suppressor, it was found that the Cu agglomeration was observed between two Ta films due to the large difference in thermal expansion between the Cu film and the Ta film. On the other hand, the SiO₂ was successfully used as a suppressor, and Cu agglomeration did not occurred even after annealing at 650 °C by the suppression of the Cu diffusion. This means that the Ta diffusion barrier deposited at \( V_s = -125 \text{ V} \) could be stable up to 650 °C without reaction between Cu and Si.
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