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RESEARCH ARTICLE ENGINEERING & TECHNOLOGY

ADHESION OF COPPER WITH DIFFUSION BARRIER LAYER FOR COPPER INTERCONNECTION

Md. Maniruzzaman*, S.M. Shamsul Alam, Md. Shamim Ahsan, Md. Tariq Hasan and A.K.M. Ahsanul Haque

Electronics and Communication Engineering Discipline, Khulna University, Khulna 9208, Bangladesh.

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Abstract: Adhesion of copper with diffusion barrier layer has been studied for Cu interconnection. Ta-based barrier materials have been employed. The Cu adhesion property with these barrier materials was estimated by stress concept, and was experimentally examined. Higher and high stresses are attained in thin Cu layer (10 nm thick) when deposited on TaN and Ta diffusion barrier layers, which lead to poorer and poor adhesion strengths with Cu, respectively. On the other hand, much lower stress are attained in the thin Cu layer when deposited on TaSiN diffusion barrier, revealing much better adhesion strength of Cu with TaSiN layer. X-ray diffraction spectra and scanning electron microscopy measurement revealed that the highly stressed thin Cu layer on TaN barrier layer changes to a low stressed thin Cu layer as a result of agglomeration, which happened after annealing at 400 °C. The surface of thin Cu layer changes to rough surfaces with annealing at 400 °C in the layer deposited on TaN. However, a smooth surface is held in the low stress layer on the TaSiN barrier layer.

Key words: Cu interconnection, electromigration, diffusion barrier, stress, adhesion

Introduction

Copper films have been employed as an interconnecting material for Si ultra-large scale-integrated (ULSI) circuits due to their low electrical resistivity and high resistance against electromigration compared to the traditional interconnecting material of aluminum. However, the electromigration problem is still a major concerning issue in Cu interconnect technology, because the current density along fine interconnects increases as interconnect dimensions are downscaled. A high current density of interconnects causes failures in electronic devices by electromigration. The mechanism of the electromigration failure in Cu interconnects has been studied on the basis of electromigration paths (Hu *et al.*, 1999; Lloyd *et al.*, 1999; Tu, 2003; Hau-Riege, 2004).

The main electromigration paths of Cu interconnect are the interface between Cu and the dielectric capping layer (e.g., SiN and SiC) and that between Cu and the diffusion barrier layer (e.g., TaN and NbN). Between these two interfaces, that between Cu and dielectric capping layer showed the poorest adhesion property. Thus, a weak adhesion between Cu and dielectric capping layer results in atomic transport at the Cu/dielectric interface and void formation (Hu *et al.*, 2001; Lane *et al.*, 2003). Recently, an improved electromigration Cu life time has been realized by introducing a metallic capping layer of Ta, CoSnP or CoWP to replace dielectric capping layer (Hu *et al.*, 2002,

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* Corresponding author: Tel: +88-01914-066284, e-mail: <m_m_zaman@hotmail.com>

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2003a, 2003b). If a metallic capping layer were adopted in Cu interconnects, the interface between Cu and the diffusion barrier can become a new main path of electromigration (Lloyd *et al.*, 1999; Hayashi *et al.*, 2003; Hu *et al.*, 2003a; Tu, 2003). Therefore, an adhesion promoter (glue layer), such as Ti, Ta or Nb, is inserted to improve the electromigration resistance (Abe and Onoda, 2003; Hayashi *et al.*, 2003; Maniruzzaman *et al.*, 2006).

Since the diffusivity is directly related to the melting point of the host material, the most frequently proposed diffusion barriers cum adhesion promoters for Cu interconnection are based on the metals which possess the highest melting points, e.g., refractory metals, such as Ta, Ti, and W, and their compounds with N, C, Si and B. As for the refractory metals, Group IVa metals (Ti, Zr, Hf) have good adhesion but these metals react with Cu. Group VIa metals (Cr, Mo, W) do not react with Cu but these metals have poor adhesion. However, Group Va metals (V, Nb, Ta) have good adhesion and they do not react with Cu. So, Ta is better barrier metal compare to the metals in Groups IVa and VIa. Ta is also better than V and Nb metals of the same group, mainly due to excellent chemical inertness at the Cu/Ta interface. The most common diffusion barriers cum adhesion promoters for Cu metallization today are Ta, TaN and TaSiN, as they offer excellent barrier properties (Tu, 2003). However, systematic explanations of the Cu adhesion property on Ta-based glue layer materials (Ta, TaN or TaSiN) are not sufficient, as reported in literature, so far.

Besides, agglomeration becomes a more serious problem in fine Cu seed layers. Agglomeration largely affects peeling of the Cu layer during chemical-mechanical polishing (CMP) as well as the orientation of the Cu (111) layer (Tu, 2003). However, origin and details of the agglomeration have not been well understood. It is also known that the adhesion strength at the Cu/barrier interface is affected largely by the stress of Cu layer. Correlation of the adhesion strength with the stress must be studied to solve the problem of peeling, which occurs frequently in the Cu CMP process.

Under these circumstances, in this paper, the adhesion of Cu to Ta-based barrier materials, i.e., Ta, TaN, TaSiN, was estimated by stress concept, and was experimentally evaluated on the basis of the agglomeration behaviors of Cu after annealing at 400 °C, and by measuring the spectrum shift angle and wetting angle of Cu on substrates (barrier layers). It is revealed that TaSiN shows the lowest stress, that is, the best adhesion characteristics than the other barrier materials, i.e., TaN, Ta, and, thus, it can be a very suitable glue layer element for Cu interconnection. These results also suggest that stress concept can be applied for selecting the best glue layer (adhesion promoter) material.

Materials and Methods

Deposition of 200 nm thick oxide layers (SiO_2) was performed on Si (100) wafers by plasma-enhanced chemical vapor deposition (PECVD). Different 30 nm thick barrier layers for Cu diffusion were deposited on the SiO_2 layer by magnetron sputtering. A Ta barrier layer was deposited from a high purity Ta target (99.99%). Polycrystalline (c-) and amorphous (a-) TaN layers were deposited by reactive sputtering using a high purity Ta target. Stoichiometry and grain size of the TaN layer were controlled with a varying flow rate ratio of N_2 gas employed in the reactive sputtering. A low Si composition TaSiN layer was made from low Si composition TaSi target by reactive sputtering. A thin Cu layer (10 nm thick) as a seed layer was deposited sequentially on these barrier layers in the same chamber by magnetron sputtering. The crystallographic orientations and the spectrum shift of the corresponding orientations of the Cu layer were examined by X-ray diffraction (XRD) measurements. Stress at the Cu/barrier interface was determined quantitatively from the shift of the XRD spectra. The interface adhesion has been assessed using a pull-off device. Variation of surface morphology was observed by scanning electron microscope (SEM).

Results

First of all, we performed the XRD measurements in the θ-2θ mode to examine the crystallographic orientations and the spectrum shift of the corresponding orientations of the Cu layer deposited on Ta-based different diffusion barriers (e.g., Ta, a-TaN, c-TaN and TaSiN). The XRD spectra obtained from Cu (10 nm)/a-TaN (30 nm)/SiO_2/Si specimens before and after annealing at 400 °C for different lengths of time are shown in Fig. 1. A weak Cu (111) peak appeared at 45.423° in the as-deposited specimen, although it should appear as a strong peak at 43.295° in a stress-free Cu layer as given by JCPDS-ICDD Card File No. 04-0836. Due to annealing at 400 °C for 10 min, a weak Cu (111) peak was observed at 43.295°, and the Cu (111) peak observed in the as-deposited specimen is still seen at 45.423° (Fig. 1). When annealing time was increased to 20 min, the spectrum of Cu (111) at 45.423° disappeared completely and the spectrum of Cu (111) at 43.295° changed to a strong peak (Fig. 1). A very small peak of Cu (200) also appeared at 50.7°, as seen in Fig. 1.

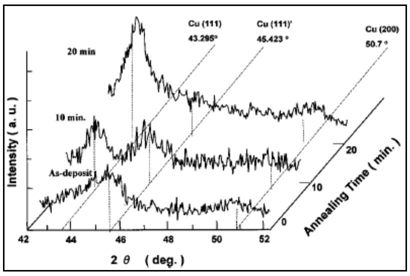

Fig. 1. XRD spectra of θ-2θ scan obtained from Cu (10 nm)/a-TaN (30 nm)/SiO_2/Si specimens before and after annealing at 400 °C for different lengths of time.

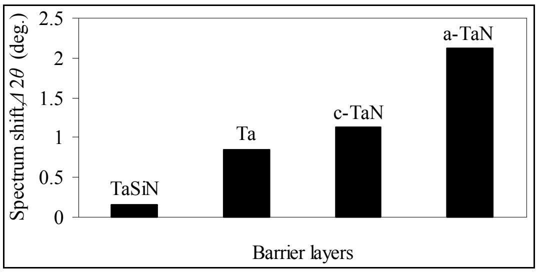

Fig. 2. Spectrum shift ($\Delta 2\theta$) of Cu (111) thin layer deposited on different barrier layers.

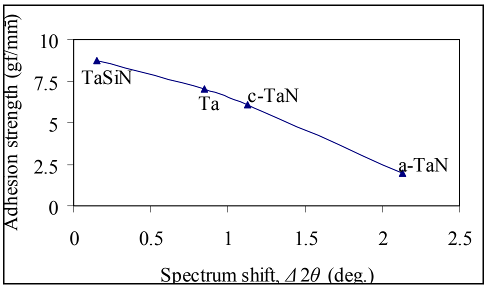

Fig. 3. Correlation of adhesion strength at Cu/barrier interface with shift angle ($\Delta 2\theta$).

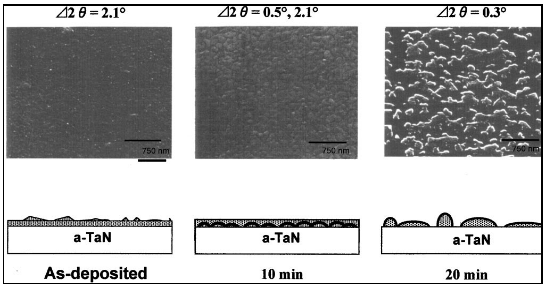

Fig. 4. SEM photographs showing surface morphologies obtained from the Cu (10 nm)/a-TaN (30 nm)/SiO_2/Si specimens before and after annealing at 400 °C for different lengths of time.

Then, spectrum shift ($\Delta 2\theta$) was determined from the XRD measurement of Cu (111) peaks of the as-deposited Cu layers for different diffusion barriers (e.g., Ta, a-TaN, c-TaN and TaSiN). The observed spectra shifted slightly to the higher angle side from an angle of 43.295° in bulk Cu (111). The measured spectrum shift ($\Delta 2\theta$) of each Cu (111) seed layer is shown in Fig. 2.

After that, adhesion strength at the Cu/barrier interface was observed quantitatively by a commercial pull-off adhesion device. Correlation of the adhesion strength at the Cu/barrier interface with the shift angle, $\Delta 2\theta$, in the XRD spectra for Cu (111) is shown in Fig. 3, where $\Delta 2\theta$ was determined in Fig. 2.

Agglomeration of a 10 nm thick Cu seed layer was studied, where a-TaN barrier layers were used. Variation of the surface morphology in the Cu seed layer with an annealing temperature of 400 °C for different lengths of time was observed by the SEM, as shown in Fig. 4. The amount of shift angle ($\Delta 2\theta$) determined in Fig. 1 is shown numerically at the top of these SEM photographs.

Discussion

As seen in Fig. 1, in the as-deposited specimen, the shift of the spectrum by 2.128° indicated the deposition of a highly stressed and weakly (111) oriented Cu seed layer. This spectrum was separated into two spectra with an increase in annealing time to 10 min. A weak peak due to the low stress Cu layer was observed at 43.295°. Spectrum for the stressed layer still appeared at 45.423°, as seen in Fig. 1. This spectrum change indicated that the layer stress is reduced with this 10 min annealing and also that a highly stressed layer still exists at the surface. When annealing time was increased to 20 min, the spectrum at 45.423° due to the stressed Cu layer disappeared completely and the spectrum at 43.295° changed to a strong peak. A small peak of Cu (200) also appeared at 50.7° (Fig. 1). These spectrum changes indicated clearly that the stress can be released sufficiently with this longtime annealing.

As also seen in Fig. 2, the spectrum shift of Cu (111) peak is very different for different barrier layers. This result shows clearly that the stress can be controlled broadly by varying the barrier layers. The stress of a thin film is directly proportional to the shift of the XRD spectra, that is, higher the spectrum shift ($\Delta 2\theta$), higher the stress. Therefore, higher and high stresses were obtained in a-TaN and c-TaN barrier layers, as higher and high spectrum shift were attained in these barrier layers, respectively (Fig. 2). This spectrum shift decreased to 0.85 when a Ta barrier layer was used. The shift of $\Delta 2\theta$ decreased to 0.15 and the lowest stress was realized when a Cu (111) seed layer was deposited on a low Si content TaSiN layer.

Empirically, peeling occurs frequently in the Cu conductive layer deposited on the TaN barrier layer. However, this peeling does not occur as frequently in the layer on a Ta barrier layer. However, correlation of the adhesion strength with the stress has not been studied much in multilevel Cu interconnections. In this study, adhesion strength at the Cu seed layer/barrier layer was observed quantitatively, and correlation of the adhesion strength with the stress given by $\Delta 2\theta$ is shown in Fig. 3. This figure shows clearly that adhesion strength is closely related with the stress of the seed layer and can be varied broadly with varying the stress. That is, the adhesion strength of the Cu layer is increased with decreasing stress. Higher and highest adhesion strengths were obtained in Ta and TaSiN barrier layers. Thus, the problem of peeling may be solved if only a low stress Cu seed layer can be deposited on a TaSiN barrier layer.

Stress relaxation and formation of a stress-free Cu layer may be achieved by agglomeration. However, agglomeration of the Cu seed layer is a serious problem in the Cu interconnection (Tu, 2003). The relationship between stress and the formation of agglomeration was studied by SEM observation for the Cu (10 nm)/a-TaN (30 nm)/SiO_2/Si contact system, and the results are depicted in Fig. 4. A very smooth surface was obtained in the as-deposited Cu layer because greater stress was attained at the interface, as given in Figs. 1 and 2. When annealing time was increased to 10 min, agglomeration occurred just at the interface. However, the surface feature was invariable and remained smooth, as seen in Fig. 4. This morphological change and XRD measurements showed that agglomeration appeared just at the interface with an a-TaN layer. This agglomeration region was broadened and the layer changed to a discontinuous layer over the whole area when annealing time was increased to 20 min, as seen in Fig. 4. It must be noted from the data in Figs. 1 and 4 that the stress-free thin Cu layer is formed as a result of the formation of agglomeration.

The wettability of Cu on the glue layer (adhesion promoter) is an important factor for electromigration resistance, because a good Cu wettability on the glue layer means high strength of Cu adhesion to glue layers. In a recent study, the strength of Cu adhesion to surrounding materials shows a linear relationship with lifetime for electromigration (Hu *et al.*, 2002, 2003a, 2003b; Abe and Onoda, 2003; Lane *et al.*, 2003). Thus, the evaluation of the strength of Cu adhesion to glue layers can be an important factor for estimating electromigration resistance. One of the simple methods to measure the strength of Cu adhesion to glue layers is the evaluation of wetting angle of Cu on glue layers. The wetting angle (α) can be defined by the force balance between the surface and interface energy of each film. Without elastic strain, Young's relationship (Smith, 1995) should be satisfied for an island in equilibrium on a planar substrate,

$$\gamma_i + \gamma_{Cu} \cos \alpha = \gamma_{glue} \qquad (1)$$

where α is the wetting angle, γ_{Cu} is the surface energy of Cu, γ_i is the interface energy between Cu and the substrate, and γ_{glue} is the surface energy of glue layer (Fig. 5).

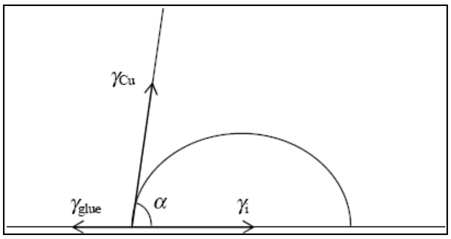

Fig. 5. Schematic diagram of an agglomerated island on glue layer.

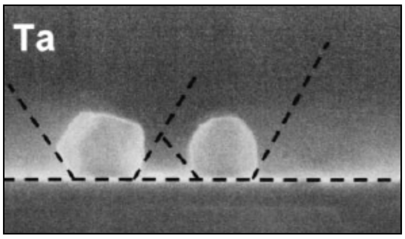

Fig. 6. A SEM image of Cu thin film on Ta layer annealed at 400 °C for 20 min, showing agglomerated island.

Adhesion energy, which represents the strength of Cu adhesion onto underlayers can be obtained as follow (Smith, 1995),

$$E_{ad} = \gamma_{glue} + \gamma_{Cu} - \gamma_i = \gamma_{Cu}(1+\cos \alpha) \qquad (2)$$

Eq. (2) indicates that the wetting angle (α) can be an index for estimating the strength of Cu adhesion onto glue layers. To measure the Cu wetting angle, the samples (i.e., for Cu on TaSiN, Ta, c-TaN and a-TaN barrier layers, respectively) were annealed at 400 °C for 20 min that is sufficient for agglomeration in a 10 nm thick Cu film (Tu, 2003). Cu wetting angle was determined from a cross-sectional SEM image (Figs. 4 and 6, for example).

The average wetting angles of Cu on the a-TaN, c-TaN, Ta and TaSiN were 149.2°±4.5°, 131.4°±4.5°, 123.3°±8.5° and 61.4°±4.6°, respectively. The relative energy of Cu adhesion to the glue layers was calculated using Eq. (2) and shown in Table 1. These results well correspond to the results of Fig. 3.

Table 1. Wetting angle of Cu on glue layers and calculated energy of Cu adhesion to glue layers.

Glue layers/Adhesion promoters	a-TaN	c-TaN	Ta	TaSiN
Wetting angle (°)	149	131	123	61
Relative adhesion energy (E_{ad})	0.14	0.34	0.46	1.48

However, in these experimental results, we observed that TaSiN showed a better Cu adhesion property than the other barrier elements, such as, TaN or Ta. And, the results obtained in this study also support the relationship between Cu adhesion and stress properties.

Even so, a question may arise on the subject of annealing temperature, i.e., is the annealing temperature 400 °C sufficient? We know that the normal device operating temperature does not usually exceed 100 °C, and, the device processing temperature is usually ~ 400 °C. Taking notice into these facts, in this study, the annealing temperature has been kept fixed at 400 °C and only the annealing time has been varied. However, this is not the end of the investigation. The authors are also investigating the effects of the higher annealing temperatures (500 ~ 600 °C, for example) for applying some special cases where, sometimes, higher annealing temperature is necessary, and, will be reported soon.

Aside from that, this paper is mainly focused on the some mechanical properties of materials for semiconductor fabrication technology. Electrical properties (electrical resistivity, or, I-V characteristics etc.) are also of great importance. This concerning issue is just left now, and, the authors has marked it as an immediate future work.

Conclusion

Stress of a thin Cu seed layer can be controlled broadly by varying the diffusion barrier cum adhesion promoter layer. In this study, higher stress was attained in the thin Cu layer on TaN barrier layer. Lower stress layer can be obtained on Ta layer. Lowest stress was attained when the layer was deposited on a low Si content TaSiN barrier layer. Stress was reduced due to annealing at 400 °C even in a highly stressed seed layer. This stress reduction is caused by the formation of agglomeration. In this study, we revealed that adhesion strength at the Cu/barrier (cum adhesion promoter) interface is closely related with the stress at the interface (Lower the stress, higher/better the adhesion and vice versa!). In this study, very low adhesion strength was attained when a-TaN was the barrier layer. Slightly better adhesion was attained in the Ta barrier layer employed. Better diffusion barrier performance and better adhesion strength were attained when a low Si content TaSiN layer was employed instead of a Ta or TaN barrier layer.

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