# 무전해도금 구리배선재료의 열적 및 접착 특성

김정식, 허은광
서울시립대학교 재료공학과

# Thermal and Adhesive Properties of Cu Interconnect Deposited by Electroless Plating

Jung-Sik Kim and Eun-Kwang Hur
*Department of Materials Science and Engineering*
*University of Seoul, Seoul 130-743, Korea*

**초 록**

본 연구에서는 무전해도금으로 증착된 구리박막의 열적 및 접착특성에 관하여 고찰하였다. Si 기판에 MOCVD 방법으로 TaN 확산방지막을 증착한 후, 무전해도금으로 구리박막을 증착하여 Cu/TaN/Si 다층구조를 제조공정하였다. 그리고, Ar 분위기에서 열처리시켰으며, 열처리온도에 따른 비저항 변화를 고찰함으로서 Cu/TaN/Si 계의 열적 특성을 분석하였다. 무전해도금 구리박막의 접착특성은 스크래치 테스트에 의해 평가하였으며, 열적 증착방법과 스퍼터 방법으로 증착된 구리 박막과 비교하였다. 스크래치 테스트 결과, 무전해도금 구리 박막의 접착력이 열적 증착과 스퍼터 방법으로 증착된 구리 박막보다 더 우수하였다.

**Abstract**

In this study, the adhesion and thermal property of the electroless-deposited Cu thin film were investigated. The multilayered structure of Cu/TaN/Si was fabricated by electroless-depositing the Cu thin layer on the TaN diffusion barrier which was deposited by MOCVD on the Si substrate. The thermal stability was investigated by measuring the resistivity as post-annealing temperature for the multilayered Cu/TaN/Si specimen which was annealed at Ar gas. The adhesion property of Cu films was evaluated by the scratch test. The adhesion of the electroless-deposited Cu film was compared with other deposition methods of thermal evaporation and sputtering. The scratch test showed that the adhesion of electroless plated Cu film on TaN was better than those of sputtered Cu film and evaporated Cu film.

## 1. Introduction

For future ICs, copper is being considered as an alternative to Al alloys [1-2] because of its low bulk elecrical resistivity and improved electromigration performance. Deposition processes of Cu metallization have been intensively studied through PVD, CVD, laser reflow, electroplating and electroless deposition, etc. According to most reported results, physical vapor deposition of Cu showed poor step coverage, while the chemical vapor deposition showed good step coverage, but somewhat showed uncertain reliability problems such as impurities, high resistivity with different processing condition. The electrochemical method of electroplating and electroless deposition has been recently considered as the prominent technique of Cu metallization owing to the development of chemical-mechanical polishing (CMP) and damascene processes in the semiconductor processing. The electroplating and electroless deposition produce high-quality Cu filling of the high-aspect ratio via contacts and lines[3-4]. Also, they shows low electrical resistivity (~1.7μΩ·cm) and excellent electromigration reliability[5].

In the present study, the adhesion and thermal properties of the electroless-deposited Cu thin film were investigated. The multilayered structure of Cu/TaN/Si was fabricated by electroless-depositing the Cu thin layer on the TaN diffusion barrier. Adhesion property of the electroless-deposited Cu film was evaluated by the scratch test. Also, the annealed Cu/TaN/Si system was analysed for the thermal stability and electrical property by using a 4-point probe, SEM, XRD and AES.

## 2. Experimental Procedures

The substrates used in the present study were p-type (100) Si wafers with resistivity of 1-100 Ω·cm. The MOCVD TaN films were deposited at the substrate temperature of 300°C using pentakis-methyl-amino-tantalum (PEMAT) as a precursor which was carried out by Ar gas into a reaction chamber at 1-torr. Next, electroless deposition of Cu on the TaN diffusion barrier was carried out by dipping in the solution bath which consists of copper sulfate, formaldehyde and minor additives. An activation treatment was performed with a dilute solution of $PdCl_2$ prior to Cu-electroless deposition, and the pH of the solution bath was controlled by adding the NaOH solution.

Adhesion of the Cu-film was evaluated by the scratch test (CSEM-Revetest) shown schematically in Fig.1. The test was conducted by drawing a stylus with diamond tip of 200 μm radius over a Cu-film under increasing vertical loads. Signals of acoustic emission and friction coefficient (μ) were detected. Film thickness and surface morphology were measured by SEM. Resistivity was measured by a four-point probe. Analysis on the thermal stability for the Si/TaN/Cu system was carried out by XRD and AES.

## 3. Results and Discussion

The deposition rate of electroless-Cu depends on the temperature and pH of solution bath. Above 12.2 or below 11.8 of pH, deposition rate was too slow and deposited surface was not homogeneous. Good surface morphology and reasonable deposition rate of 2 μm/hr was obtained at the pHs ranging 11.8~12.2 at 32°C. The adhesion of Cu-film on TaN was examined by a scratch test. Three types of Cu films on TaN/Si substrate were prepared by electroless deposition, sputtering and evaporation methods. Fig.2 shows the variations of acoustic emission with increasing load for Cu films deposited by elecroless deposition, sputtering and evaporation, respectively. As shown in the figure, the critical de-adhesion load taken as the onset of large acoustic emission is higher in order of electroless deposition, evaporation and sputtering from 1.8 to 2.2. Fig.3 is the optical micrograph of scratch track showing the overall appearance of scratch film.

And Fig.4 is the SEM micrograph showing the detailed cracks initiated along the scratch track. Through optical and SEM micrographic observations, cracks were found to occur around 6 N load at which the friction coefficient also began to increase significantly. From the micrograph observation and the variation of friction coefficient, the critical loads required to scribe away the Cu-film were determined to be 5.96 N, 5.80 N, and 5.80 N for electroless deposition, sputtering and evaporation, respectively. Consequently, adhesion of the electroless deposited Cu-film on TaN evaluated by the scratch test was better than those of the sputtered and evaporated Cu-films.

Cu/TaN/Si specimens were annealed in Ar-atmosphere in order to understand the effect of annealing at inert atmosphere. Fig.5 shows AES depth profiles for Cu/TaN/Si specimens as deposited, annealed at 400°C and 600°C in Ar gas. The specimen annealed at 600°C shows significant inter-diffusion of either Cu or Si through the TaN layer. Fig.6 shows the resistivity for Cu/TaN/Si specimens annealed in Ar gas for 30min. Slow increase up to 550°C is due to the formation of $Cu_2O$ compounds by reacting with minor impurity of oxygen in Ar gas whose content was observed to be about 100 ppm by the yttria-stabilized zirconia(YSZ) oxygen sensor. Rapid increase above 600°C is due to the intermixing of Cu and Si through the TaN layer as shown in the results of AES depth profiles of Fig.5.

## 4. Conclusions

The adhesion and thermal properties of the electroless-deposited Cu thin film on the TaN diffusion barrier were investigated. Thermal stability of Cu/TaN/Si system was maintained up to the annealing temperature of 550°C in Ar atmosphere above which the intermediate compound of Cu-Si was formed through diffusion into the TaN layer. The adhesion of the electroless deposited Cu-film on TaN evaluated by the scratch test was better than those of the sputtered and evaporated Cu-films.

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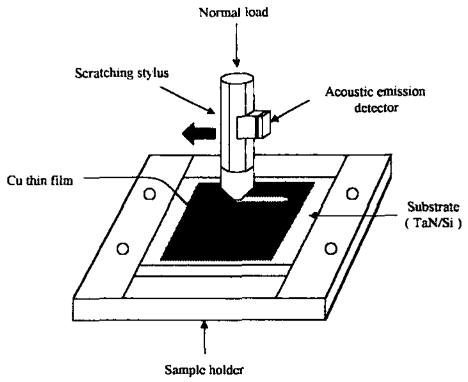


Fig. 1. Schematic diagram of scratch test.

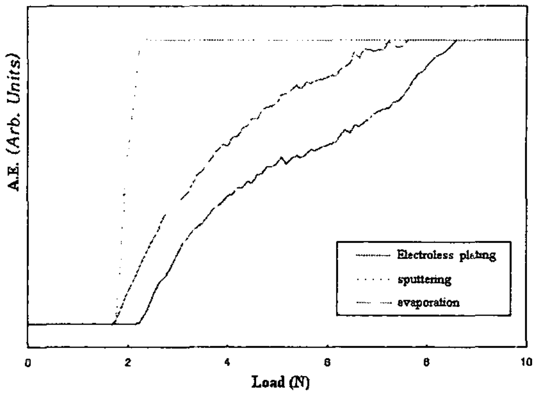


Fig. 2. A.E.(Acoustic Emission) of the scratch test.

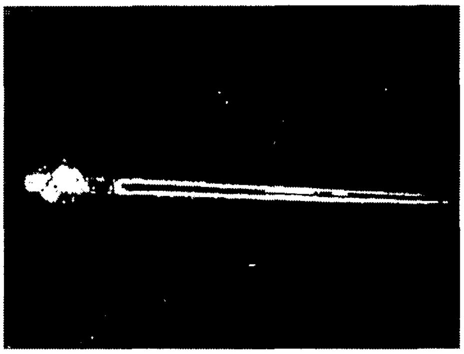

Fig. 3. Optical micrograph of the scratch track.

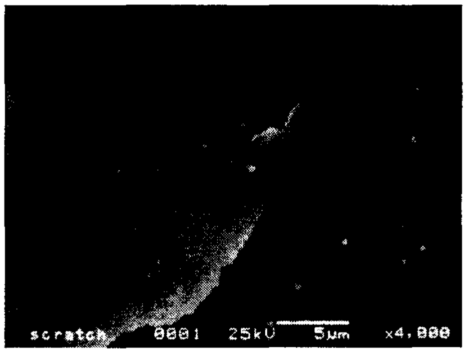


Fig. 4. SEM micrograph of crack on the scratch track.

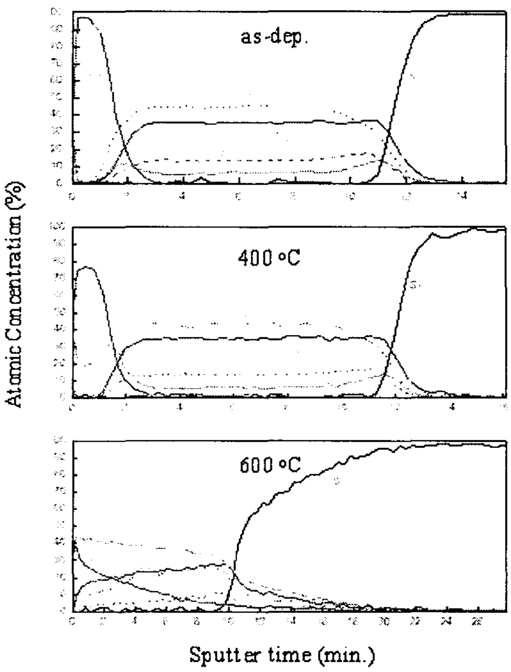


Fig.5. AES depth profiles for Cu/TaN/Si systems.

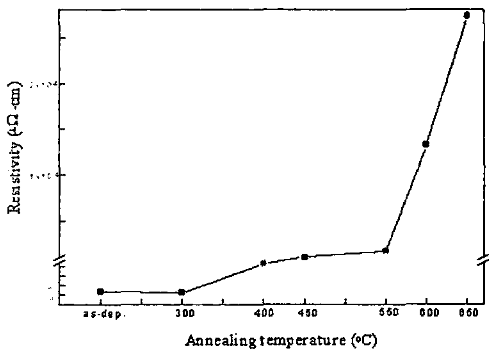


Fig.6. Dependence of the resistivity of the Cu/TaN/Si System.