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Barrier capability of TaN_x films deposited by different nitrogen flow rate against Cu diffusion in $Cu/TaN_x/n^+$–p junction diodes

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Abstract

This paper investigates the barrier capability of tantalum nitride (TaN_x) layers against Cu diffusion. The TaN_x layers were reactively sputtered in contact holes to a thickness of 50 nm by using a different nitrogen flow rate. Results indicate that the TaN_x layers fail to be a diffusion barrier due to a relative high resistivity for nitrogen flow ratios exceeding 10%. In addition, we found that the phase of α-Ta(–N) functions as an effective barrier against Cu diffusion and that Cu/TaN(3–5%)/n^+–p junction diodes are able to sustain a 30 min furnace anneal up to 500°C without causing degradation of the electrical characteristics. The high-temperature failure of barrier capability for the TaN_x layers is due to interdiffusion of Cu and Si across the TaN_x film structure to form Cu_3Si. The surface roughness and the film structure of TaN_x layers determine the ability of Cu and Si interdiffusion. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion barrier; Copper; Tantalum; Cu_3Si

1. Introduction

A high performance interconnection network on a chip is becoming increasingly important for ultralarge-scale integration (ULSI) of Si integrated circuits. Continued shrinking of devices has led to a discrepancy between the device and interconnect performance. The obvious advantages for using Cu as interconnect material to substitute aluminum alloys are related to improving the operation speed and the reliability of ULSI circuits [1,2]. Compared with aluminum alloys, Cu provides a lower bulk resistivity, higher electro-migration and stress-migration resistance, higher melting point, and lower reactivity with commonly used diffusion barrier materials [3,4]. Unfortunately, Cu has drawbacks that retard its widespread application, such as problems of dry etching, poor adhesion to oxide and other dielectric materials, easy oxidation in air, and fast diffusion in Si and oxide even at room temperature, resulting in degradation of the device characteristics [5,6]. However, if an appropriate diffusion barrier between Cu and its underlying layers is provided, Cu will satisfy the needs of future integrated circuits.

Recently, Cu has been used for global (long distance) interconnect. It is known that the variation of Cu sheet resistance with anneal temperature provides a good measure of barrier capability for the Cu/barrier/dielectric system. Furthermore, with continued shrinking of the devices, the local (short distance) interconnects will also change to a Cu metallization system to match the improving performance of ULSI circuits. For the local interconnect, Cu is directly connected to the source/drain area of MOSFETs and the variation of Cu sheet resistance with anneal temperature is no longer a good criterion for evaluating the barrier capability of the Cu/barrier/Si system. Although much research has been

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devoted to evaluate the barrier capability by the measurement of Cu sheet resistance, few literature is available on the measurement of junction leakage of Cu contacted p–n junctions [7,8]. Hence the objective of this research is to examine the reliability of Cu metallization for local interconnect.

Many diffusion barriers against Cu diffusion have been examined extensively in recent years [9–14]. Among them, tantalum nitride (TaN_x) is by far the most common diffusion barrier for Cu because of the absence of any compounds between Cu and Ta, and also Cu and N [15–17]. In addition, the reaction temperature of possible silicide formation at the barrier/Si interface can be raised to a higher value, as compared with Ta/Si, by adjoining Ta atoms to Si as a compound in the form of a nitride [18]. Several researchers have investigated that the phase of TaN_x films sequentially formed by sputtering Ta under increasing amounts of nitrogen partial flow includes tetragonal metastable phase Ta (β-Ta), nitrogen-incorporated cubic Ta (α-Ta(–N)), hexagonal Ta_2N and NaCl-type TaN [19,20] However, in most of the studies the barrier capability of TaN_x films has been determined by material analysis. In this paper, we investigate the barrier capability of TaN_x films deposited at various nitrogen flow ratios during reactive sputtering by electrical properties and material characteristics. Meanwhile, we compare the variation of junction leakage with the variation of Cu sheet resistance for Cu/TaN_x/p–n junctions as the anneal temperature is changed. Our results may help to clarify whether the Cu sheet resistance or the junction leakage is a suitable measure of the diffusion capability of TaN_x films against Cu diffusion for the Cu/barrier/Si system.

2. Experimental procedure

The barrier capability of TaN_x films against Cu diffusion was investigated using a structure of Cu/TaN_x/n^+–p junction diodes. The key feature of this experiment is the different nitrogen flow rate during reactive sputtering of TaN_x formation. First, p-type (1 0 0)-oriented Si wafers with a resistivity of 6–9 Ω cm were used in this study. After standard RCA cleaning, the wafers were administered the LOCOS process to define active regions. The n^+–p junctions were formed by As^+ implantation at 60 keV with a dose of 5×10^{15} cm^{-2} followed by the rapid thermal annealing (RTA) process at 1050°C for 30 s in N_2 ambient. After the contact windows were cleaned by dipping sample in HF, a reactively sputtered TaN_x film of 50 nm thick was deposited onto the active regions with different nitrogen flow ratio. In this paper, nitrogen flow ratio is defined as a ratio of N_2 partial flow to total gas flow (N_2 + Ar) and the deposited TaN_x film is denoted as TaN (%). For example, TaN (5%) is a TaN_x film reactively sputtered by 5% nitrogen flow ratio. Then Cu film with a thickness of 300 nm was deposited subsequently in the same sputtering system without breaking vacuum. During the sputtering, gas pressure was maintained at 6 mTorr with a power selected at 500 and 1500 W for TaN_x and Cu, respectively. Finally, Cu and TaN_x layers were patterned by dilute HNO_3 and Cl_2 plasma respectively for the formation of Cu/TaN_x/n^+–p junctions.

To investigate the barrier capability of TaN_x films against Cu diffusion, the devices were thermally annealed at a temperature ranging from 400°C to 600°C for 30 min in a vacuum of 10^{-3} Torr. For electrical analysis, the leakage current of the diodes was measured by a HP4145B semiconductor parameter analyzer at a reverse bias of −5 V. The sheet resistance (R_s) of the Cu films was determined by the 4-point probe measurement. In addition, X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), and atomicforce microscope (AFM) were used for material analysis.

3. Results and discussion

Fig. 1 shows the resistivity of the reactively sputtered TaN_x films as a function of nitrogen flow ratio. In this figure, pure β-Ta with a resistivity of 197 μΩ cm is observed without any nitrogen flow. As seen in this figure, the resistivity of TaN_x films initially decreases with increasing nitrogen flow ratio and reaches a minimum value of 159 μΩ cm for 5% nitrogen flow ratio. This is due to the change of phase from β-Ta to α-Ta(–N) and β-Ta exhibits a higher resistivity than nitrogen incorporated α-Ta [21]. On the contrary, the resistivity of TaN_x films increases slightly between nitrogen flow ratio of 5% and 10% and then increases dramatically for nitrogen flow ratio exceeding 10%. Fig. 2 shows the XRD spectra of TaN_x films deposited at different nitrogen flow ratios on the Si substrates. It is known that the crystallographic structure of TaN_x film is affected by nitrogen flow ratio during the reactive sputtering [22,23]. As seen in Fig. 2, diffraction patterns taken from the Ta film can be indexed to a β-Ta (tetragonal) structure. At the nitrogen flow ratio of 3%, the XRD spectrum shows a α-Ta(–N)(bcc) preferred orientation. Although the α-Ta (–N) peak is not prominent, it is still observed for the films at nitrogen flow ratios of 5%, 7%, and 10%. This indicates that the films were mainly composed of amorphous-like materials. When nitrogen flow ratio increases to 15%, NaCl-type TaN(1 1 1) and weak amorphous Ta_2N(1 0 1) peaks were observed. As nitrogen flow ratio is further raised up to 25%, the NaCl-type TaN peak predominates and becomes broader in the XRD spectra for the films with the nitrogen flow ratio higher than 25%. Since the resistivity of TaN(1 1 1) and Ta_2N are larger than that of α-Ta(–N), hence the

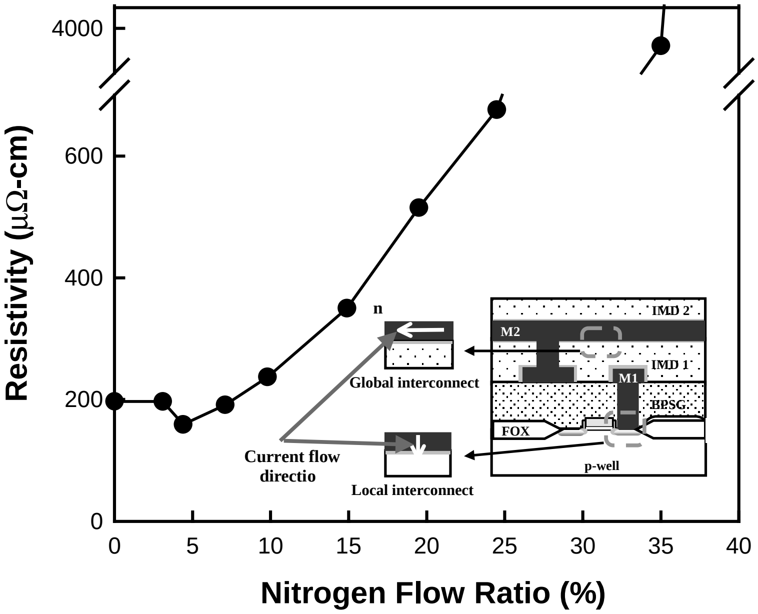


Fig. 1. Resistivities of the reactively sputtered TaN_x films as a function of nitrogen flow ratio. The inset is the cross-sectional view of the multi-level interconnection for integrated circuits.

resistivity of TaN_x increased dramatically for nitrogen flow ratios exceeding 10% as shown in Fig. 1. It should be noticed that although current flows in the $Cu/TaN_x/$dielectric system is horizontal type and the current flow path in TaN_x is in parallel with the Cu path, while for the $Cu/TaN_x/Si$ system, the current path is a vertical type and TaN_x resistance is in series to Cu (see the inset of Fig. 1). Because the series resistance of TaN_x layer in the $Cu/TaN_x/$junction diodes depends on both the resistivity and film thickness of TaN_x. In this paper, the resistivity of TaN_x is thought to be a relative high value for the nitrogen flow ratio exceeding 10% (with a TaN thickness of 50 nm). Decreasing the barrier thickness may lead to a higher acceptable range of resistivity while the thinner barrier will result in the poor barrier capability. Therefore, when TaN_x is used as a diffusion barrier between Cu and Si, the thickness and resistivity of TaN_x film should be formed as small as possible. The results shown in Figs. 1 and 2 suggest that NaCl-type TaN(1 1 1) or Ta_2N(1 0 1) (nitrogen flow ratio exceeds 10%) is not suitable as a diffusion barrier for the $Cu/TaN_x/Si$ system due to the relative high resistivity.

The variation of Cu sheet resistance as a function of the annealing temperature is commonly used to examine the capability of diffusion barrier against Cu diffusion. The difference of sheet resistance between the annealed and as-deposited samples, normalized to the sheet resistance of as-deposited samples, is called the variation percentage of sheet resistance ($\Delta R_s/R_s$ %) and is defined as follows:

$$\frac{\Delta R_s}{R_s}\% = \frac{R_{s,\text{after anneal}} - R_{s,\text{as-deposited}}}{R_{s,\text{as-deposited}}} \times 100\%$$

It is well known that Cu diffuses fast in Si and forms Cu–Si compounds at a temperature as low as 200°C. The formation of Cu–Si compounds results in the sheet resistance of Cu/Si increase. Fig. 3 illustrates the variation percentage of sheet resistance vs. annealing temperature for the $Cu/TaN_x/Si$ samples with nitrogen flow ratio ranging from 0% to 10%. In this figure, the $Cu/TaN_x/Si$ samples remain stable in the measurement of sheet resistance following anneal at temperature up to 650°C ($\Delta R_s/R_s$ % slightly decrease with increasing temperature due to the defect healing by thermal annealing). However, drastic increases in sheet resistance are found after annealing above 700°C. The drastic increase in sheet resistance is attributed to the formation of Cu_3Si precipitates from the XRD measurement (to be shown later in Fig. 4). On the other hand, as nitrogen flow ratio exceeds 15%, there was the appearance of peeling which happened for Cu films deposited on the TaN_x films after 600°C annealing. Fig. 4 shows the XRD spectra for Cu/Ta/Si and Cu/TaN(5%)/Si samples subjected to anneal at various temperatures. The diffraction patterns reveal that the two structures remain unchanged after anneal at temperature up to 600°C, while different sets of peaks belonging to Cu_3Si, Ta_5Si_3, and $TaSi_2$ are found after 700°C annealing. The high-resistivity Cu_3Si formation and related Cu decrease resulted in the drastic increases of sheet resistance as shown in Fig. 3. As seen in Fig. 4(b), peak intensity of Cu_3Si for the Cu/TaN(5%)/Si

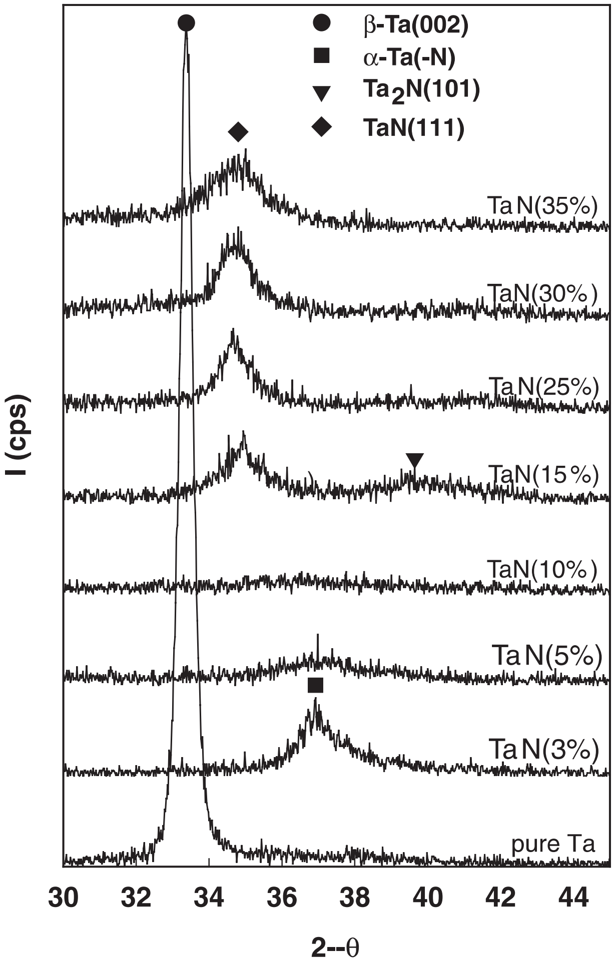


Fig. 2. XRD spectra for TaN_x deposited at various nitrogen flow ratios.

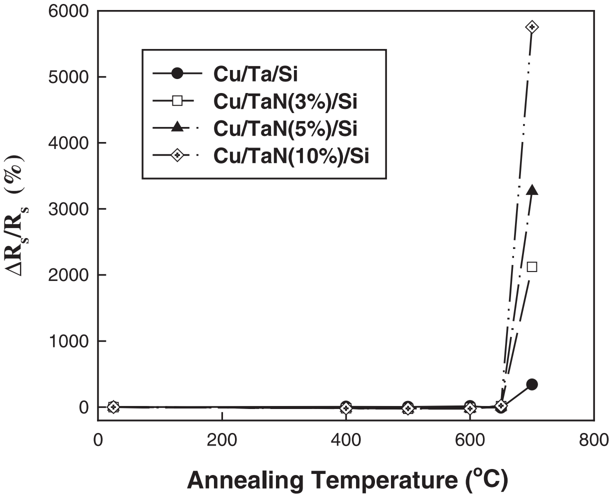


Fig. 3. Variation percentage of sheet resistance against annealing temperature for the Cu/TaN_x/Si samples.

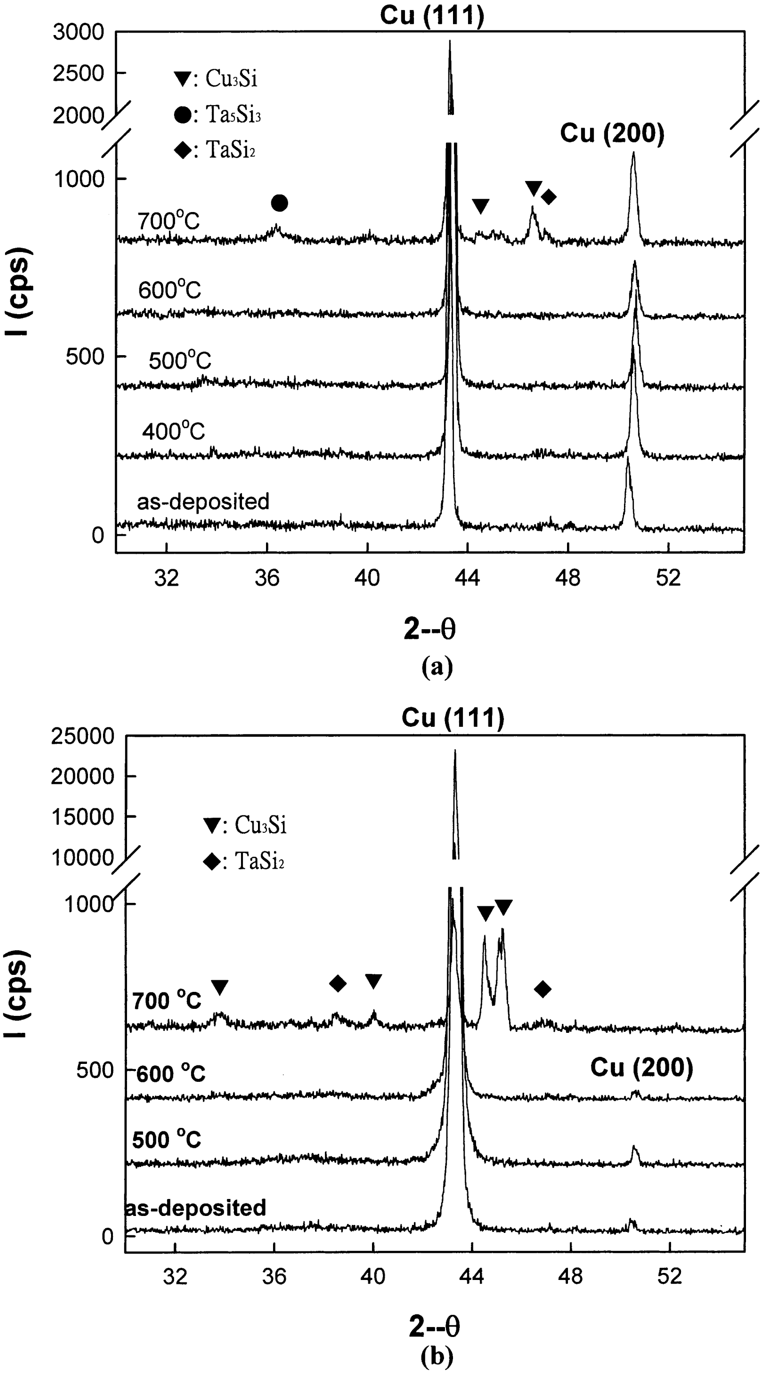


Fig. 4. XRD spectra for the (a) Cu/Ta/Si and (b) Cu/TaN(5%)/Si samples subjected to anneal at various temperatures.

sample is larger than that observed for the Cu/Ta/Si sample shown in Fig. 4(a). Hence, the fact that variation percentage of sheet resistance increases as nitrogen flow ratio increases when annealed at 700°C (see Fig. 3) may be due to the different amount of Cu_3Si formation. On the other hand, it had been reported that Cu(1 1 1) provides higher electro-migration resistance than that of Cu(2 0 0) [24]. In our experiment, the ratio of Cu(1 1 1) to Cu(2 0 0) for Cu film deposited on the TaN(5%) layer was 315.72 (23050/73) while the ratio of Cu(1 1 1) to

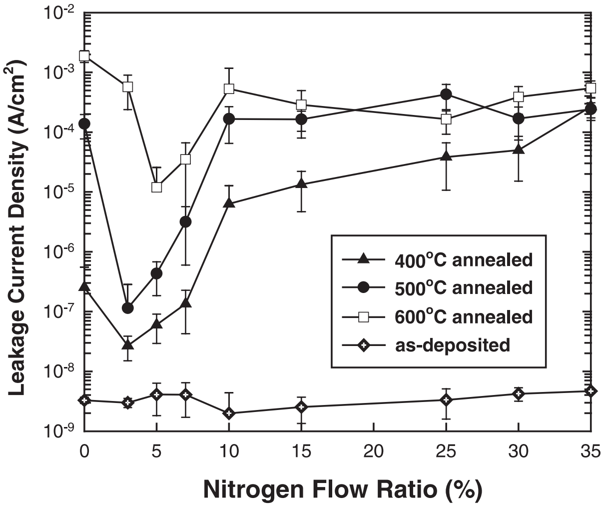
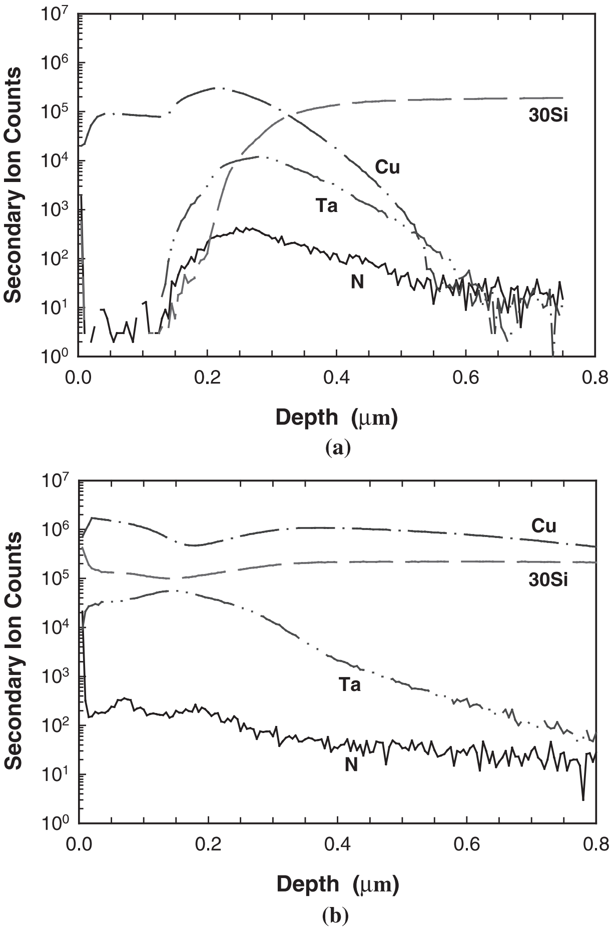


Fig. 5. Leakage current densities of the Cu/TaN$_x$/n$^+$–p junction diodes vs. nitrogen flow ratio at various annealing temperatures. Leakage current densities of the as-deposited sample (without any heat treatment) are also included for comparison.



(a)

(b)

Fig. 6. SIMS profiles of the Cu/TaN(5%)/Si sample after (a) 500°C, (b) 700°C annealing.

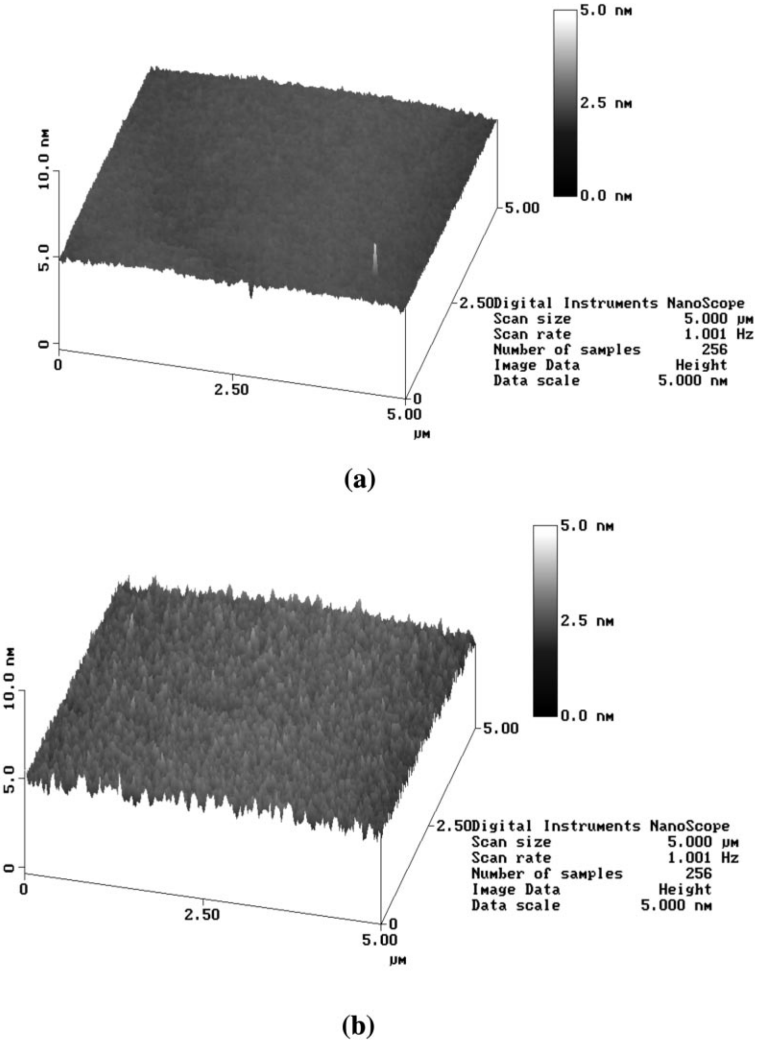


Fig. 7. AFM micrographs of TaN_x films at the nitrogen flow ratios of (a) 5%, (b) 15%, and (c) 25%.

Cu(2 0 0) on the Ta layer was 6.18 (1780/288). These results imply that TaN (5%) is a suitable diffusion barrier for the Cu metallization system from the views of resistivity, expected electro-migration resistance, and thermal stability. For further analyzing the thermal stability, SEM images were used to examine the surface morphologies of Cu film after thermal treatments. The Cu films remained stable on different diffusion barrier (TaN_x with different nitrogen flow ratios) until anneal at temperature up to 650°C. This is consistent with the results of sheet resistance and XRD measurements. Moreover, an increase in annealing temperature led to a change in color of Cu surface and a production of precipitates. For example, the smaller Cu grain of about 1.5 µm in diameter under 650°C annealing and Cu–Si compound of bigger grain of about 6 µm in diameter after 700°C annealing were observed for the Cu/Ta/Si sample. From the XRD spectra shown in Fig. 4, it is believed that the precipitates are Cu_3Si phase.

Although the results of sheet resistance, XRD, and SEM measurements show that the Cu/TaN_x/Si samples remain stable as annealed up to 650°C, the junction characteristics of Cu/TaN_x/p–n junction are necessary for evaluating the barrier capability of TaN_x against Cu diffusion. Fig. 5 illustrates the reverse-biased current densities of the Cu/TaN_x/n^+–p junction diodes with different nitrogen flow ratios under different annealing temperatures. In this measurement, the leakage current densities were obtained from an average value of 25 samples and the diode area was 1000×1000 μm^2. For the diodes without any heat treatment (as-deposited), the leakage current densities remain stable (below 10

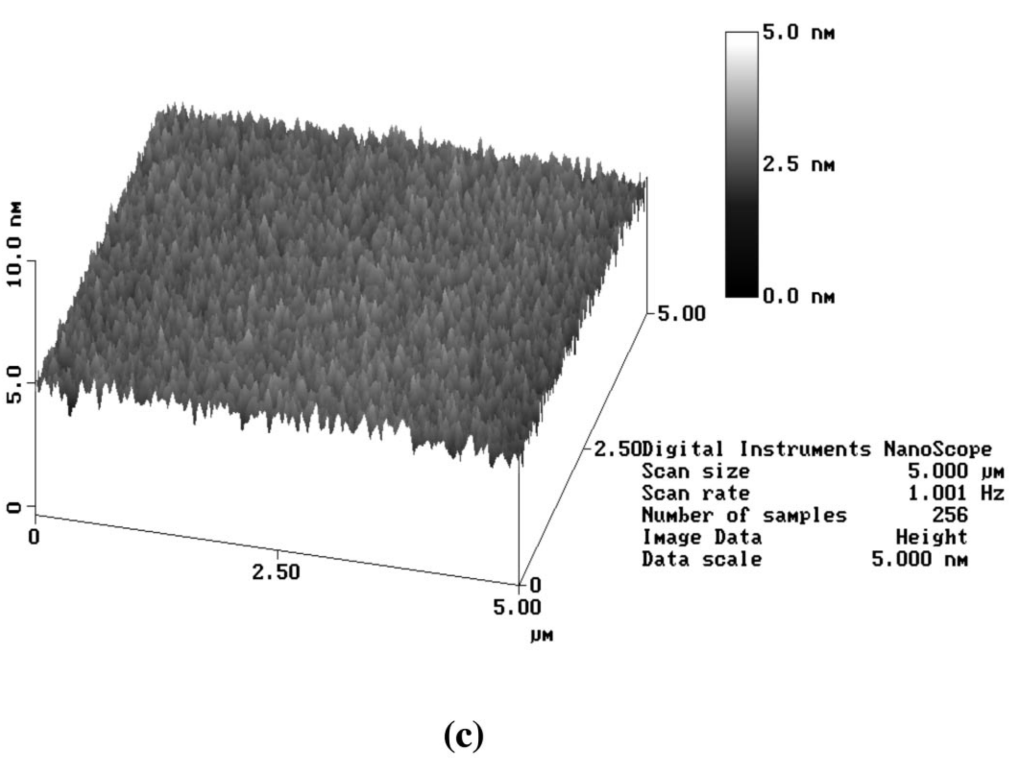


Fig. 7. (*Continued*)

nA/cm^2) as nitrogen flow ratio is increased. Nevertheless, the diode leakage increases with increasing the annealing temperature and most of diodes are degraded after annealing at 600°C. As seen in Fig. 5, the leakage current densities initially decrease, reaching a valley of minimum at 3% (for 400°C and 500°C annealing) or 5% (for 600°C annealing) nitrogen flow ratio, and then increase with increasing the nitrogen flow ratio. In other words, for the TaN (3%) and TaN (5%) diffusion barriers, the diodes endure thermal annealing at temperature up to 500°C. For the TaN$_x$ films with nitrogen flow ratios exceeding 10%, the devices all failed (defined by a criteria of 10^{-6} A/cm^2 leakage current density) after 400°C annealing. According to the XRD results as shown in Fig. 2, our data provide the evidence that the α-Ta(–N) thin film is a suitable barrier against Cu diffusion and the barrier capability of α-Ta(–N) is more effective than the β-Ta, Ta$_2$N, and TaN films. Moreover, the barrier capability of TaN(1 1 1) (15–25% of nitrogen flow ratio) is even inferior to the β-Ta(0 0 2) thin film.

SIMS and AFM measurements were used to investigate the failure mechanism of the fabricated diodes. As shown in Fig. 6(a), an interdiffusion of Cu and Si across the barrier film is found for the Cu/TaN(5%)/Si sample annealed at 500°C. After 500°C annealing, although the small amount of Cu atoms diffused into Si substrate does not affect the Cu sheet resistance significantly (see Fig. 3), the junction leakage measurement shows a two order of magnitude increase in the leakage current measurement (from 10^{-9} to 10^{-7} A/cm^2, as seen in Fig. 5) for the Cu/TaN(5%)/n$^+$–p junction diodes. Therefore, it implies that the sheet resistance measurement is only valid for the global interconnections and the junction leakage evaluation is a suitable method for local interconnections. As seen in Fig. 6(b), the large amount of interdiffusion between Cu and Si after 700°C annealing are observed by SIMS measurement, indicating that the reaction of Cu with Si results in the drastic increase of Cu sheet resistance. In addition, surface roughness of the TaN$_x$ films was examined by AFM on unpatterned samples. Fig. 7 shows the AFM images of TaN$_x$ films deposited on Si substrate with the nitrogen flow ratio of 5%, 15%, and 25%, respectively. A fairly smooth surface with a root-mean-square (RMS) value of 0.135 nm is obtained for the TaN (5%) sample as shown in Fig. 7(a). Furthermore, increasing the nitrogen flow ratio led to deposition of relatively rough surface of TaN_x films. RMS of 0.286 and 0.328 nm were obtained for nitrogen flow ratios of 15% and 25%, respectively, as shown in Fig. 7(b) and (c). Since the larger RMS of TaN_x films corresponds to a rougher interface and may have led to the poor barrier capability against Cu diffusion, these AFM results support the electrical measurements that junction leakage of the diodes increases with nitrogen flow ratio when samples were thermally annealed. In addition to the surface roughness, the barrier capability of TaN_x films may be affected by the bulk structure of TaN_x films. With increasing the nitrogen flow ratio, it is known that the evolution of structure of the TaN_x films follows the zone model to progressively change from voided columnar (Ta), through fibrous of reduced grains (α-Ta(–N)), featureless structure (Ta_2N), and finally to columnar structure (TaN) [23]. The quasi-amorphous structure of α-Ta(–N) films lengthen the diffusion path of Cu to react with Si, hence the TaN(3–5%) films provided a better barrier capability against Cu diffusion.

4. Conclusion

The barrier capability of TaN_x layers against Cu diffusion by different nitrogen flow ratio was investigated. We found that the resistivity of TaN_x films increases drastically for nitrogen flow ratios exceeding 10% and the high-resistivity TaN_x films are not suitable for the use of Cu/TaN_x/Si system. When Cu/TaN_x/n^+–p junction diodes were annealed up to 600°C, TaN-(0–10%) functions as an effective barrier against Cu diffusion for the sheet resistance measurement, while most of samples failed in the junction leakage evaluation. Results suggest that the junction leakage is more suitable for evaluating the barrier capability of TaN_x films on the Cu/TaN_x/n^+–p junction diodes than the variation of sheet resistance. In this paper, Cu/TaN(3–5%)/n^+–p junction diodes are able to retain their integrity in electrical characteristics up to 500°C annealing. The high-temperature failure of barrier capability for the TaN_x films is presumably due to the interdiffusion of Cu and Si, forming Cu–Si related precipitates, and the interdiffusion may be enhanced by the microstructure and resulting roughness of TaN_x surface.

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