

Improving the Electrical Integrity of Cu–CoSi₂ Contacted n⁺p Junction Diodes Using Nitrogen-Incorporated Ta Films as a Diffusion Barrier

Wen Luh Yang, Wen-Fa Wu, Hsin Chiang You, Keng-Liang Ou, Tan Fu Lei, *Member IEEE*, and Chang-Pin Chou

Abstract—The study on improving the electrical integrity of Cu–CoSi₂ contacted-junction diodes by using the reactively sputtered TaN_x as a diffusion barrier is presented in this paper. In this study, the Cu(300 nm)–CoSi₂(50 nm)/n⁺p junction diodes were intact with respect to metallurgical reaction up to a 350 °C thermal annealing while the electrical characteristics started to degrade after annealing at 300 °C in N₂ ambient for 30 min. With the addition of a 50-nm-thick TaN_x diffusion barrier between Cu and CoSi₂, the junction diodes were able to sustain annealing up to 600 °C without losing the basic integrity of the device characteristics, and no metallurgical reaction could be observed even after a 750 °C annealing in furnace. In addition, the structure of TaN_x layers deposited on CoSi₂ at various nitrogen flow rates has been investigated. The TaN_x film with small grain sizes deposited at nitrogen flow ratios exceeding 10% shows better barrier capability against Cu diffusion than the others.

Index Terms—Cobalt, copper, diffusion barrier, junction, nitrogen, tantalum.

I. INTRODUCTION

FOR A long time, metal silicides had proven valuable to both ohmic and Schottky contacts. Aside from applications as ohmic or Schottky contacts, high conductivity metal silicides were proposed in 1979 as contacts to doped polysilicon or polycide structure to reduce resistance and give extra interconnection capability [1]. In 1981, the concept was extended to diffusion areas by forming self-aligned silicide at both polysilicon and diffusion areas simultaneously for improving both contact and interconnects [2]. Silicide-related technologies have therefore become an integral part of submicron devices in recent years.

The current trend in shrinking integrated circuits to improve the performance of chips requires substituting copper (Cu) for aluminum as interconnects in the deep submicron-integrated circuits [3], [4]. Recently, copper has been used as the global interconnect material for ultralarge-scale integration (ULSI) cir-

cuits as a replacement for aluminum due to its very low electrical resistivity and excellent electromigration resistance [5]. In the near future, copper will also be used in short-distance local interconnects for high-speed ULSI circuits.

It is well known that Cu forms Cu–Si compounds at very low temperatures (200 °C) [6] and also introduces deep level traps in silicon, a phenomenon that deteriorates device performance [7]. Therefore, the realization of thermally stable Cu-contacted systems suppressing mass transport over interface due to the high diffusivity and reactivity of Cu is an essential issue in the use of Cu as a local interconnect material. Since copper is directly in contact with the source–drain area of MOSFETs in the local interconnects, it is expected that direct contact between copper and metal-silicided junction is inevitable. In recent years, CoSi₂ has received a lot of attention due to its superior characteristics, compared to TiSi₂, on issues of phase transformation, bridging effect, and chemical stability [8]. Unfortunately, Cu was found to diffuse across the silicide layer and form the Cu–Si compound below the silicide layer in the Cu–CoSi₂–Si systems [9], [10]. Because the reaction in the Cu–silicide–Si structure occurs at a relatively low temperature, an effective diffusion barrier layer is required for the application of the Cu–silicide–Si structure.

The diffusion barriers employed directly in between the Cu and Si have been widely investigated in recent years. Various barrier layers for the Cu diffusion, such as refractory metals (Ta, W, Mo, Ti, and Cr) and their nitrides, have been developed [11]–[16]. Among these materials, tantalum (Ta) has been extensively investigated as a diffusion barrier for Cu since it not only shows relatively high melting temperature of 3087 °C but is also shown to be thermal stable with respect to Cu. In addition, it was reported that the barrier capability of Ta films against Cu diffusion could be improved by incorporating nitrogen into Ta films using the reactive sputtering technique [15], [16]. In the TaN_x–Si system, several researchers have investigated that the phase of TaN_x films sequentially formed by sputtering Ta under increasing amounts of nitrogen partial flow includes the tetragonal metastable phase Ta (β -Ta), nitrogen-incorporated cubic Ta [α -Ta(-N)], hexagonal Ta₂N, and NaCl-type TaN [16]. In the Cu–Ta_xN_x/n⁺p junction diodes, the α -Ta(-N) structure with reduced grains functioned as an effective barrier against Cu diffusion [16]. In this study, we used the TaN_x barrier to improve the electrical integrity of the Cu–CoSi₂ contacted junction diodes. Besides, with increasing the nitrogen flow ratio, the evolution of structure of the TaN_x films reactively sputtered on CoSi₂ films were investigated.

Manuscript received April 24, 2002. This work was supported in part by the National Science Council, Taiwan, R.O.C., under Contract NSC-90-2215-E-035-007 and the Feng Chia University (FCU-RD-88-01). The review of this paper was arranged by Editor R. Shrivastava.

W. L. Yang is with the Department of Electronic Engineering, Feng Chia University, Taichung, Taiwan, R.O.C. (e-mail: wlyang@fcu.edu.tw).

W.-F. Wu is with National Nano Device Laboratories, Hsinchu, Taiwan, R.O.C.

H. C. You and T. F. Lei are with the Institute and Department of Electronics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

K.-L. Ou and C.-P. Chou are with the Institute and Department of Mechanical Engineering, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

Digital Object Identifier 10.1109/TED.2002.804692

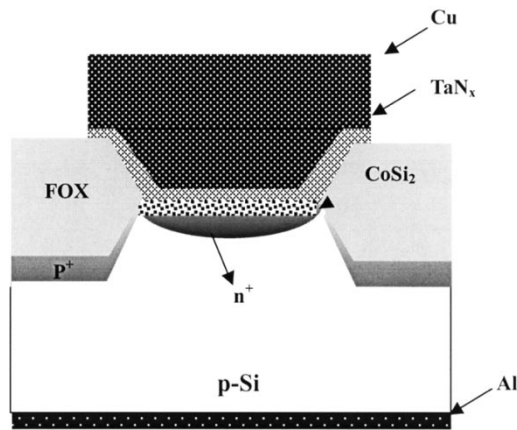


Fig. 1. Cross-sectional view of the Cu-TaN_x-CoSi₂/n⁺-p junction diodes.

II. EXPERIMENTAL PROCEDURE

The substrates used in the experiments were 6-in, p-type, (100)-oriented silicon wafers with a resistivity of 6~9 Ω-cm. After standard RCA cleaning, the wafers were administered to the LOCOS process to define active region. The n⁺-p junctions were formed by As⁺ implantation at 60 keV with a dose of $5 \times 10^{15} \text{ cm}^{-2}$ followed by the rapid thermal annealing (RTA) at 1050 °C for 30 s in N₂ ambient. After the junctions were formed, a layer of cobalt (Co) 15 nm thick was deposited first and then followed by deposition of a TiN film (30 nm) that was used to prevent oxidation of cobalt. A two-step annealing process was used to form CoSi₂. The first annealing step was carried out at 500 °C for 30 s in N₂. The silicide-forming reaction occurs whenever the silicon and metal are in contact, that is, on the contact window. The unreacted cobalt and TiN films were selectively removed in a piranha solution (H₂SO₄:H₂O₂:H₂O in the 1:1:5 volume ration). The second step of annealing was performed at 750 °C for 30 s to achieve low resistivity CoSi₂ films. After the CoSi₂ film was formed, a 50-nm-thick TaN_x film was deposited onto the contact windows by reactively sputtering tantalum target in N₂ + Ar mixture. In this experiment, the nitrogen flow ratio is defined as the ratio of N₂ partial flow to the total gas flow (N₂ + Ar) and the deposited TaN_x film is denoted as TaN_x(×%). For example, TaN_x(10%) is the TaN_x film reactively sputtered by 10% nitrogen flow ratio. Then a Cu film 300-nm-thick was subsequently deposited in the same sputtering system without breaking vacuum. During sputtering, the pressure was maintained at 6 mtorr, and the sputtering power was 500 W and 1500 W for TaN_x and Cu, respectively. The Cu pattern was defined and etched using dilute HNO₃ solution, while the TaN_x film was etched using Cl₂ plasma to form Cu-TaN_x-CoSi₂/n⁺-p junction diodes. The cross-sectional view of the fabricated diodes is shown in Fig. 1. Finally, the samples were thermally annealed at a temperature ranging from 200 °C to 800 °C for 30 min to investigate the electrical characteristics.

III. RESULTS AND DISCUSSION

A. Cu-CoSi₂-Si Contact System

The sheet resistance R_s of the Cu-CoSi₂-Si structure after thermal annealing in N₂ for 30 min at various temperatures

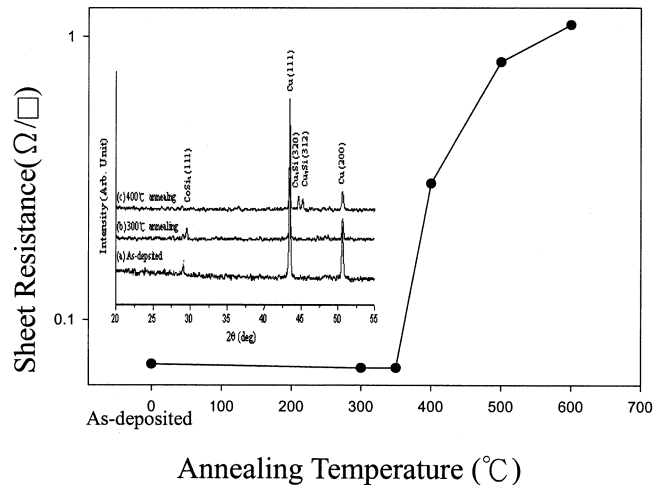


Fig. 2. Sheet resistance versus annealing temperature for the Cu-CoSi₂-Si sample. The inset shows the XRD spectra of the Cu-CoSi₂-Si structure.

is shown in Fig. 2. Several results have indicated that Cu diffuses fast in Si and forms Cu-Si compounds at temperatures as low as 200 °C [6], [7]. The formation of Cu-Si compounds results in the increase of the measured sheet resistance values. The sheet resistance of Cu(300 nm)-CoSi₂(50 nm)-Si structure remains stable for anneal at temperatures up to 350 °C. (The AES depth profile also indicates that no apparent structure intermixing occurred in the Cu-CoSi₂-Si structure up to 350 °C annealing.) Just like Al, Cu reacts at relatively low temperatures with silicides and Si [9], [10]. A sharp increase of sheet resistance was observed after annealing at 400 °C, indicating a structural change had occurred after this annealing. The inset of Fig. 2 shows the glancing angle (3°) X-ray diffraction (XRD) results. It reveals that Cu₃Si phase has formed after annealing at 400 °C. The formation of high-resistivity Cu₃Si and related in decrease Cu result in the drastic increase in sheet resistance, as shown in Fig. 2.

The reverse leakage current density of Cu-CoSi₂/n⁺-p junction diodes measured at -5 V for 20 randomly chosen samples is illustrated in Fig. 3. It is seen that although the Cu film in the Cu-CoSi₂-Si structure keeps intact up to 350 °C thermal annealing from the sheet resistance, XRD, and AES measurements, the junction starts to degrade after 300 °C annealing from the diode characterization. The leakage current increases further with increased annealing temperature. SIMS (secondary ion mass spectroscopy) measurement was used to investigate the failure mechanism of the fabricated diodes. Results showed that a small amount of interdiffusion of Cu and Si is found for the sample annealed at 300 °C. At this stage, the junction has failed and the leakage current densities were on the order of 10⁻⁴ A/cm². On the contrary, the volume fraction of the Cu₃Si phase is too small to be detected by the XRD measurement. Thus, the sheet resistance of Cu-CoSi₂-Si sample is not significantly affected by the relatively small interdiffusion as shown in Fig. 2. 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 the local interconnections of Cu-metallization scheme.

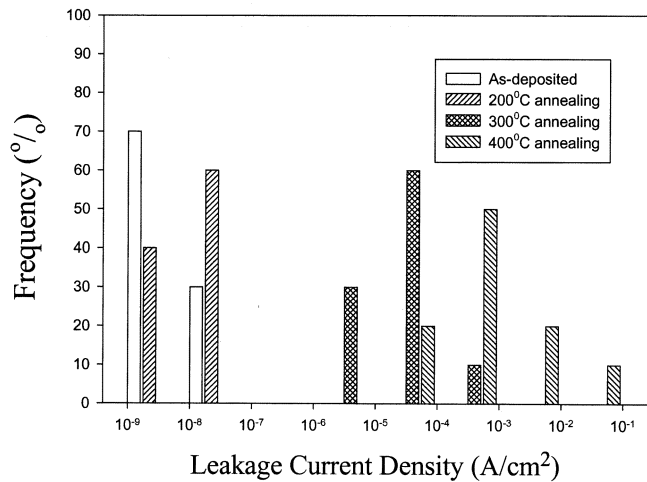


Fig. 3. Histograms showing the distributions of leakage current density of the Cu-CoSi₂/n⁺-p junction diodes under various annealing temperatures.

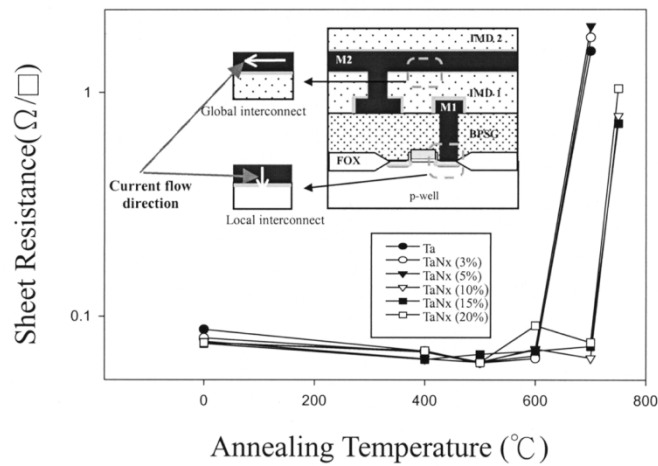


Fig. 4. Sheet resistance versus annealing temperature for the Cu-TaN_x-CoSi₂-Si sample. The TaN_x layer was reactively sputtered at the nitrogen flow ratio ranging from 0% to 20%. The inset is the cross-sectional view of the multilevel interconnection for integrated circuits.

B. Cu-TaN_x-CoSi₂-Si Contact System

Although Fig. 2 shows that with a 50-nm thick film of CoSi₂ between Cu and Si, the electrical properties of junction diodes not affected after annealing at 350 °C. However, this temperature is not high enough for the back-end requirement of ULSI processing. We therefore, used the TaN_x diffusion barrier to improve the electrical integrity of the Cu-CoSi₂ contacted junction diodes. Fig. 4 shows the sheet resistance versus the annealing temperature for the Cu-TaN_x-CoSi₂-Si samples, where the TaN_x barrier layer was deposited by the nitrogen flow ratio ranging from 0% to 20%. It is seen that with the addition of the diffusion barrier reactively sputtered at nitrogen flow ratios of 0%, 3%, and 5% in that order between Cu and CoSi₂, the sheet resistance of Cu(300 nm)/TaN_x(50 nm)-CoSi₂(50 nm)-Si structures does not change up to 600 °C furnace annealing. However, a drastic increase in sheet resistance was found after annealing above 700 °C. The drastic increase in sheet resistance is attributed to the

formation of Cu₃Si precipitates from the XRD measurement (see Fig. 6). Besides, as the nitrogen flow ratio exceeds 10%, the sheet resistance of Cu-TaN_x-CoSi₂-Si samples was stable up to 700 °C furnace annealing. A sharp increase of sheet resistance was observed after annealing at 750 °C, indicating a structure change had occurred at this temperature. The sheet resistance measurement results indicate that TaN_x layers with N₂ flow ratios above 10% on CoSi₂ are more effective barriers against Cu diffusion. As seen the inset of Fig. 4, it should be noticed that current flows in the Cu-barrier-dielectric system (long-distance global interconnection) is a horizontal type and the current flow path in the barrier layer is in parallel with the Cu path, while for the Cu-barrier-Si system (short distance local interconnection), the current path is a vertical type and the TaN_x resistance is in series to Cu. It is reported that the resistivity of reactively sputtered TaN_x films initially decreased with increasing nitrogen flow ratio and reached a minimum value of 159 μΩ-cm for 5% nitrogen flow ratio, then increased slightly between the nitrogen flow ratios of 5% and 10% and increased dramatically as the nitrogen flow ratio exceeding 10% [16]. Increasing the nitrogen ratio (>10%) in the reactively sputtered TaN_x films may lead to a higher barrier capability against Cu diffusion while the higher nitrogen flow rate will result in the highly resistivity of the TaN_x films.

The SEM micrographs for the CoSi₂ surface after removal of the Cu and TaN_x layers by the HNO₃ + H₂O₂ (1 : 1) solution are shown in Fig. 5. After 700 °C annealing, precipitates were found on the CoSi₂ surface for the Cu-TaN_x(0% and 5%)-CoSi₂-Si samples as shown in Fig. 5(a) and (b), while the surface of CoSi₂ remains intact for the Cu-TaN_x(10%)-CoSi₂-Si sample as shown in Fig. 5(c). This implies that the barrier capability of TaN_x layers against Cu diffusion in the Cu-TaN_x-CoSi₂-Si structure increased with increasing the N₂ flow rate during the reactive sputtering. However, the 800 °C thermal annealing [Fig. 5(d)] reveals precipitate formation on the CoSi₂ surface for the Cu-TaN_x(10%)-CoSi₂-Si sample which is consistent with the results of sheet resistance measurement as shown in Fig. 4.

Fig. 6 shows the XRD spectra for the Cu-TaN_x-CoSi₂-Si samples subjected to anneal in N₂ for 30 minute at various temperatures. For the TaN_x films deposited at the nitrogen flow ratio of 0% and 5%, the diffraction patterns reveal that the samples remain unchanged after anneal at temperatures up to 600 °C, while different sets of peaks belonging to Cu₃Si, TaSi₂, and Ta₅Si₃ are found after 700 °C annealing as shown in Fig. 6(a) and (b). The cross-sectional TEM micrographs have showed that most of the Cu transported across the barrier and CoSi₂ layers and reacted with Si substrate, resulting in the drastic increase of sheet resistance as shown in Fig. 4. In the meanwhile, the cross-sectional TEM measurement indicates that the CoSi₂ layer did not dissociate during the process of the high-temperature annealing, implying the Si of Cu₃Si, TaSi₂, and Ta₅Si₃ comes from the Si substrate. Another series of XRD patterns presented in Fig. 6(c) and (d) indicates the samples (TaN_x films deposited at the nitrogen flow ratio of 10% and 20%) remain unchanged after anneal at a temperature up to 700 °C. But intermetallic compounds were also observed on the structure of Cu-TaN_x(10%~20%)-CoSi₂-Si samples after

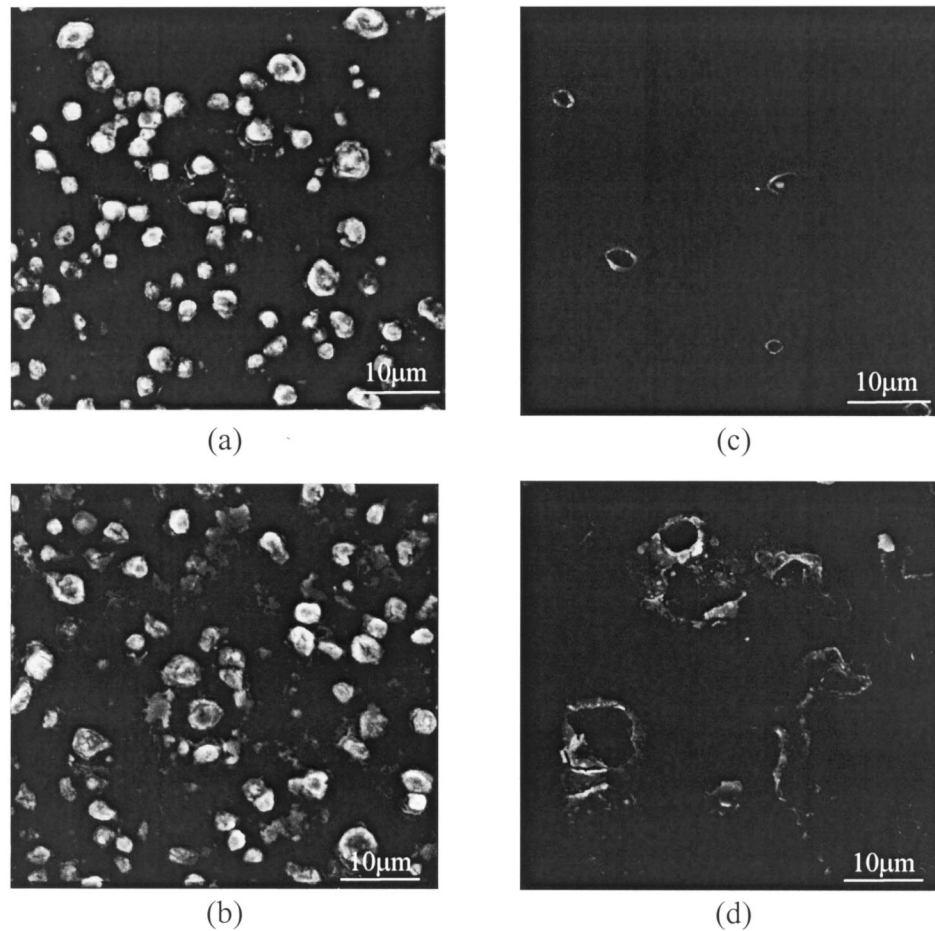


Fig. 5. SEM micrographs of CoSi_2 after removal of the Cu and TaN_x films from the Cu- TaN_x - CoSi_2 -Si samples. The sputtered TaN_x films and the annealing temperatures are (a) TaN_x (0%), 700 °C; (b) TaN_x (5%), 700 °C; (c) TaN_x (10%), 700 °C; and (d) TaN_x (10%), 800 °C, respectively.

800 °C annealing. The annealing temperatures resulted in the abrupt increase of sheet resistance as shown in Fig. 4, consistent with the results of SEM in Fig. 5. The results of Figs. 4 and 6 show that the annealing temperature before the Cu- CoSi_2 -Si samples become unstable increased from 350 °C to 600 °C with the addition of a 50 nm thickness of TaN_x (0%~5%) as a barrier between Cu and CoSi_2 . Increasing the nitrogen flow rate during the sputtering of TaN_x films will lead to a higher barrier capability of the TaN_x films and the failure annealing temperature for the Cu- TaN_x (10%~20%)- CoSi_2 -Si samples is further increased to 700 °C.

In our previous investigation [16], the XRD pattern for different Ta and TaN_x films deposited on (100) silicon substrate under different nitrogen flow rates follows the zone model, which progressively changed from voided columnar film of Ta, through fibrous of reduced grains [α -Ta(-N)], featureless structure (Ta_2N), and finally to columnar structure (TaN). The quasi-amorphous structure of α -Ta(-N) films lengthen the diffusion path of Cu before it can react with Si, hence the TaN_x (3~5%) films provided a better barrier capability against Cu diffusion than those of TaN_x (0% and 10~30%) films [16]. Fig. 7 shows the XRD spectra of the TaN_x films deposited at the various nitrogen flow ratios on the CoSi_2 film. Just like the TaN_x deposited on the Si, the crystallographic structure of TaN_x film deposited on the CoSi_2 was also affected by

the nitrogen flow ratio during the reactive sputtering. In this figure, tetragonal β -Ta is observed without any nitrogen flow. By incorporating nitrogen into the Ta films, the relatively low resistivity as measured from the four-point probe along with the phase identified by XRD patterns clearly indicates that the deposited films of nitrogen flow ratios of 3% and 5% are the low-resistivity α -Ta phase and nitrogen-doped body-centered cubic (bcc) α -Ta(-N) phases, respectively. The diffraction pattern for the films deposited at the nitrogen flow ratio of 10, 15, and 20% respectively contains the high-resistivity face-centered cubic (fcc) TaN_x phase. In contrast to the TaN_x films deposited on the Si substrate, these patterns indicate that all the deposited films are not composed of an amorphous-like structure.

The bright-field image and selective area diffraction indicated that grain sizes of the TaN_x films deposited on the CoSi_2 film decreased with the increased nitrogen flow ratio. Fig. 8(a) displays a transmission electron bright-field micrograph, taken from the diffuse ring of the diffraction pattern (inset) for β -Ta films with grain size of 20~30 nm deposited without any nitrogen flow. On the contrary, the matrix exhibits a speckle feature of size ~2 nm for TaN_x films deposited at 20% nitrogen flow ratio [Fig. 8(b)]. The activation energies of the Cu diffusion in the TaN were measured to be 1.3 eV~2.7 eV, which indicated that the Cu diffusion in the TaN would be controlled

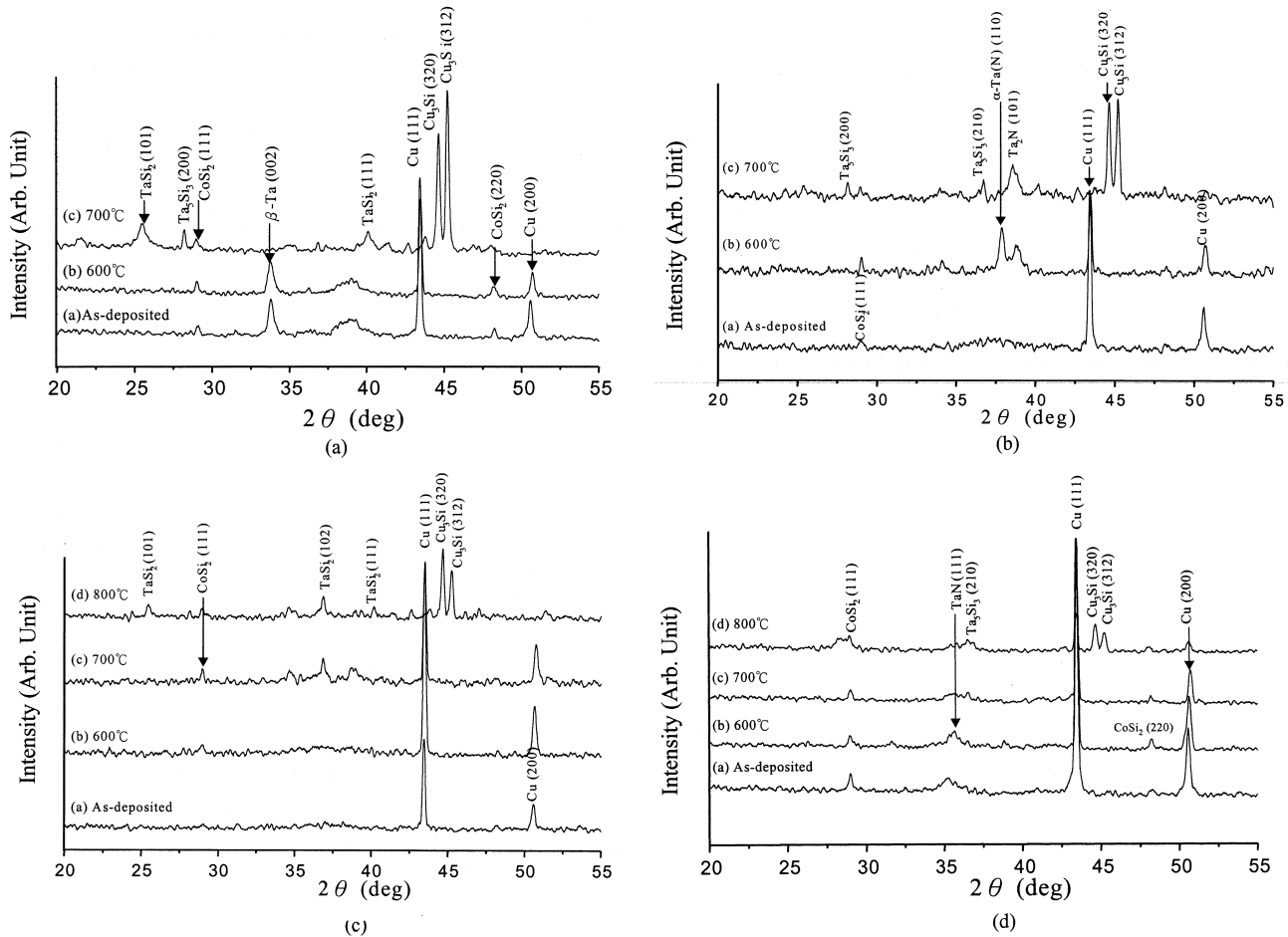


Fig. 6. XRD spectra for (a) Cu–Ta_x(0%)–CoSi₂–Si; (b) Cu–Ta_x(5%)–CoSi₂–Si; (c) Cu–Ta_x(10%)–CoSi₂–Si; and (d) Cu–Ta_x(20%)–CoSi₂–Si samples subjected to anneal at various temperatures.

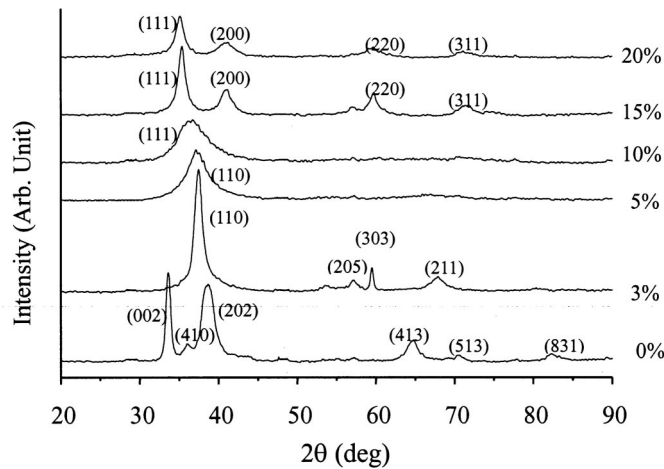
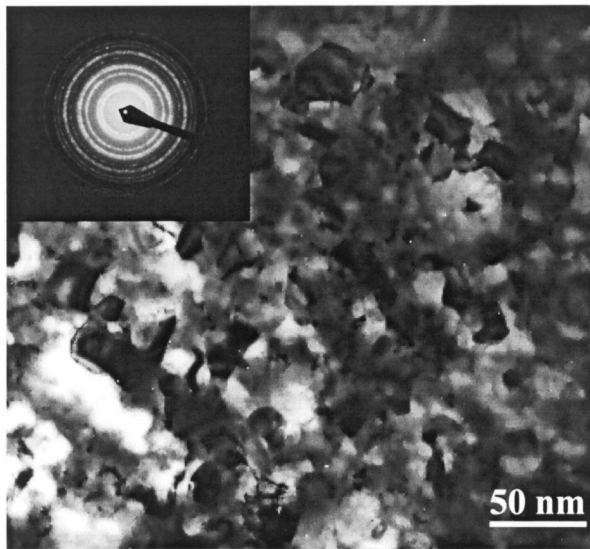


Fig. 7. XRD spectra of the Ta_x deposited at the various nitrogen flow ratios on CoSi₂. The phase identified by XRD patterns indicates that the deposited films of nitrogen flow ratios of 0, 3, and 5% are the β-Ta phase, α-Ta phase, and nitrogen-doped bcc-α-Ta(-N) phases, respectively. The diffraction pattern for the films deposited at the nitrogen flow ratios of 10, 15, and 20% respectively contains the fcc-Ta_x phase.

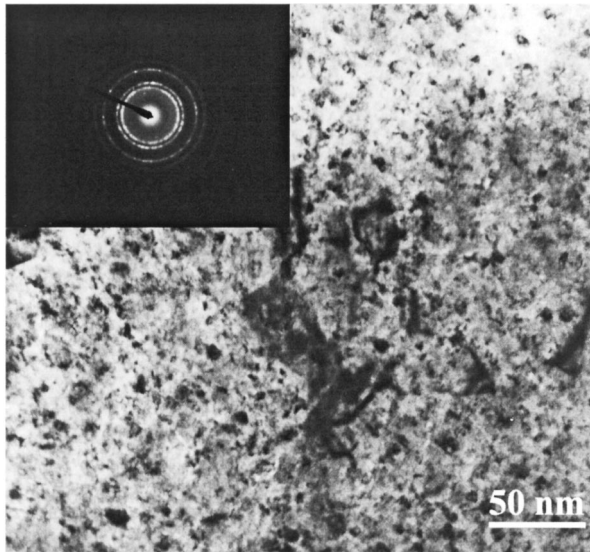
by grain boundaries and lattice diffusion [13]. Since the barrier layer allows Cu to preferentially penetrate through the grain

boundaries, a barrier structure with small grains increases the diffusion path of Cu to react with Si. Hence the Ta_x films deposited at the nitrogen flow ratio of 10%~20% yield the better barrier properties than those of 0%~5%.

As discussed in the Cu–CoSi₂/n⁺–p junction diodes, the electrical characteristics are usually more sensitive than the metallurgical properties for the analysis of the reaction that occurred within the structure. Fig. 9 illustrates the reverse-biased current densities of the Cu–Ta_x–CoSi₂/n⁺–p junction diodes annealed at various temperatures. For the diodes without any heat treatment (as-deposited), the leakage current densities remain stable on the order of 10⁻⁸ A/cm². Nevertheless, the diode leakage increased with increasing the annealing temperature and all of diodes failed after annealing at 650 °C. The abrupt increase of leakage current density in the 650 °C-annealed diodes implies that the junctions were markedly destroyed even though no evidence of reaction can be found by the material analysis. As seen in Fig. 9, it is interesting that in the 600 °C-annealed diode the barrier capability of Ta_x layer against Cu diffusion increased with increasing the nitrogen flow ratio. In other words, a 50-nm Ta_x (nitrogen flow ratio >10%) layer is observed to be an effective diffusion barrier up to 600 °C between Cu and CoSi₂ for maintaining the electrical integrity of the junction diodes. While at the



(a)



(b)

Fig. 8. Bright-field images of TaN_x films deposited at nitrogen flow ratio of (a) 0% and (b) 20%.

same annealing temperature, the diodes failed with the TaN_x diffusion barrier sputtered at the nitrogen flow ratios ranging from 0% to 5%. SIMS measurement was used to investigate the failure mechanism of the fabricated diodes. Results showed that an interdiffusion of Cu and Si across the barrier film is found for the Cu-Ta-CoSi₂-Si sample annealed at 600 °C. The electrical evaluation reveals that this interdiffusion destroyed the junction characteristics as shown in Fig. 9. In addition, the SIMS analysis for the Cu-TaN_x(5%)-CoSi₂-Si sample annealed at 600 °C showed that the relatively small amount of Cu atoms diffuses into the Si substrate as compared to the Cu-Ta-CoSi₂-Si sample. Although the small amount of Cu atoms diffused into Si substrate did not affect the Cu sheet resistance significantly (see Fig. 4), the junction leakage showed a three-order of magnitude increase in the leakage current

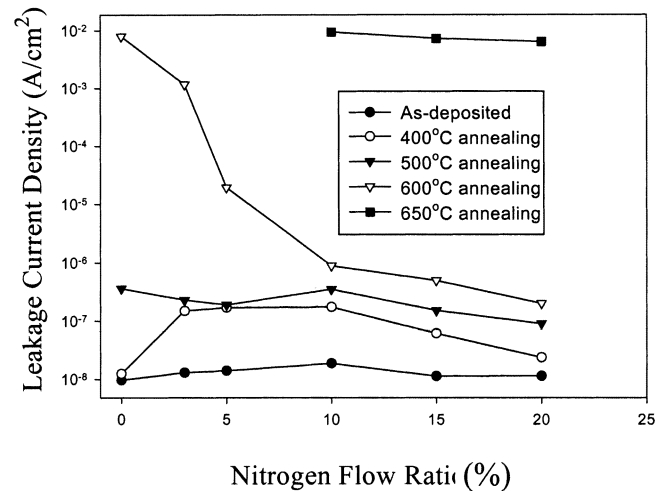


Fig. 9. Leakage current density of the Cu-TaN_x-CoSi₂/n⁺-p junction diodes versus the annealing temperature. The TaN_x layer was reactively sputtered at the different nitrogen flow ratios.

measurement (from 10⁻⁸ to 10⁻⁵ A/cm², as seen in Fig. 9). Furthermore, SIMS measurement was also used to investigate the interdiffusion for the Cu-TaN_x(>10%)-CoSi₂-Si samples annealed at 600 °C. In the measurement, an insignificant penetration of Cu atoms through the barrier film resulted in the integrity of junction characteristics. The results of SIMS analysis are consistent with the electrical evaluations. They suggest that the barrier capability of TaN_x films against Cu diffusion increased with increased nitrogen-flow rate during the reactive sputtering. Again, it should be noticed that although increasing the nitrogen flow rate will lead to a higher barrier capability of the TaN_x layer against Cu diffusion, the high nitrogen ratio results in the high resistivity of the TaN_x films. From the XRD measurement and junction characterization, results show that the crystallographic structure and the barrier capability against Cu diffusion of TaN_x films are not only dependent on the nitrogen ratio but also on the substrate type.

IV. CONCLUSION

Metallurgical reaction in Cu-CoSi₂-Si structure was observed after a 400 °C furnace annealing, while the electrical degradation of Cu-CoSi₂/n⁺-p junction diodes was observed after annealing at 300 °C. By using a 50 nm thickness of TaN_x layer as diffusion barrier, the Cu-TaN_x-CoSi₂/n⁺-p junction diodes were able to sustain the 30 min thermal annealing up to 600 °C without degrading the basic electrical characteristics. With a higher temperature annealing of 750 °C, metallurgical reaction occurred in local spots with the formation of Cu₃Si, TaSi₂, and Ta₅Si₃. 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 and the interdiffusion is affected by the microstructure of the TaN_x films. By increasing the nitrogen flow ratio, the evolution of structure of the TaN_x films changes from pure β-Ta through low-resistivity α-Ta phase, nitrogen-doped body-centered cubic α-Ta(-N) phase, and finally to small grain size face-centered cubic TaN_x phase. Among them, the small grain size face-centered cubic TaN_x

structure deposited at the nitrogen flow ratio exceeding 10% showed the better barrier capability against Cu diffusion than the others. Although increasing the nitrogen ratio (>10%) in the reactively sputtered TaN_x films may lead to a better diffusion barrier against Cu, the higher nitrogen ratio will result in the highly resistivity of the TaN_x films. Hence, when the TaN_x films are reactively sputtered at the different nitrogen flow rate as the barrier against Cu diffusion, a tradeoff between the barrier capability and resistivity of the diffusion barrier is very important for copper metallization in short distance local interconnects for the high-speed ULSI circuits. Furthermore, the crystallographic structure and the barrier property of TaN_x films are not only dependent on the nitrogen flow rate but also on the infrastructure during the deposition process.

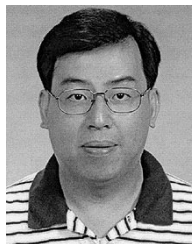
ACKNOWLEDGMENT

The authors would like to thank the National Nano Device Laboratory, Hsinchu, Taiwan, R.O.C., for providing an excellent processing environment.

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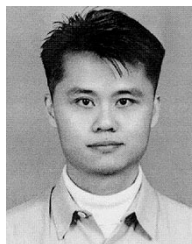
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Wen Luh Yang was born in Taichung, Taiwan, R.O.C., on May 5, 1961. He received the B.S. degree from the Department of Electrophysics, National Chiao-Tung University (NCTU), Hsinchu, Taiwan, in 1983, and the M.S. and Ph.D. degrees in electronics from NCTU, in 1987 and 1992, respectively.

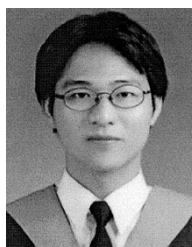
In 1993, he joined the Faculty of Feng Chia University, Taichung, Taiwan, where he is now a Professor and Chairman with the Institute and Department of Electronic Engineering. He is interested in fabrication process in deep submicrometer VLSIs, thin-gate dielectrics, ultra-shallow junctions, metal silicides, and multilevel interconnections. He is currently developing the Si–Ge gate engineering and the integration of Cu metallization and ultrashallow junctions. He is a Patent Examiner with the Intellectual Property Office, Ministry of Economic Affairs, Taiwan.

Dr. Yang has been Editor of the *Journal of Vacuum Science Technology* since 1999 and is a member of the Vacuum Science Technology Society, Taiwan.



Wen-Fa Wu was born in Kaohsiung, Taiwan, R.O.C., in 1967. He received the B.S. degree in electronics engineering from National Chiao Tung University, Hsinchu, Taiwan, in 1990, and the Ph.D. degree from Institute of Electronics, National Chiao Tung University, in 1994.

He joined the National Nano Device Laboratories (NDL), Hsinchu, as an Associate Researcher since 1994. He is engaged in developing metallization technology on IC manufacturing. His research interests include conductor systems of Cu and Al metallization, salicide technology, electromigration and stress migration, and integration of Cu and low-k dielectrics.



Hsin Chiang You was born in Changhua, Taiwan, R.O.C., on May 23, 1977. He received the B.S. and M.S. degrees in electrical engineering from Feng Chia University, Taichung, Taiwan, in 1999 and 2001, respectively. He is currently pursuing the Ph.D. degree at National Chiao-Tung University, Hsinchu, Taiwan.

His research interests include the integration of Cu metallization, electronic materials analyses, and advanced photolithography technologies.



Keng-Laing Ou was born in Kaohsiung, Taiwan, R.O.C., on December 6, 1973. He received the B.S. degree from the Department of Mechanical Engineering, and the M.S. degree in material science and engineering and mechanical engineering from National Chiao-Tung University, Hsinchu, Taiwan, in 1995 and 1997, respectively, where he is currently pursuing the Ph.D. degree.

His research includes the integration of Cu metallization, electronic materials analyses, and thin-film technologies.



Tan Fu Lei (M'98) was born in Keelung, Taiwan, R.O.C., on September 17, 1944. He received the B.S. degree in electrical engineering from National Cheng Kung University, Tainan, Taiwan, in 1967, and the M.S. and Ph.D. degrees in electronics engineering from National Chiao Tung University, Hsinchu, Taiwan, in 1970 and 1979, respectively.

From 1970 to 1972, he was with the Fine Products Microelectronics Corporation, Taiwan, as an Engineer working on the fabrication of small-signal transistors. From 1980 to 1982, he was the Plant Manager,

Photronic Corporation, Taiwan. In 1983, he joined the Faculty at National Chiao Tung University as an Associate Professor with the Department of Electronics Engineering and the Institute of Electronics. From 1984 to 1986, he was the Director of the Semiconductor Research Center. From 1991 to 1998, he also was the Deputy Director of the National Nano Device Laboratory. Presently, he is a Professor with the Department of Electronics Engineering and the Institute of Electronics. His research interests are semiconductor devices and VLSI technologies.



Chang-Pin Chou received the B.S. degree in physics from Fu Jen University, Taiwan, R.O.C., in 1971, and the M.S. degree in physics from Montana State University, Bozeman, in 1973. He then received the M.S. and Ph.D. degrees in material science and engineering from the University of Tennessee, Knoxville, in 1975 and 1978, respectively.

Since 1983, he has been a Professor with the Department of Mechanical Engineering, National Chiao-Tung University, Hsinchu, Taiwan. In 1989 and 1990, he was an International Fellow with the Department of Materials, Stanford Research Institute, Stanford, CA. He has conducted research in welding design, weldability testing, automated and robotic welding, and failure analysis. His present research interests include MEMS fabrication, thin-film materials and analyses, interconnection reliability in metallization, micro weldability, and heat treatment of metal alloys.