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Diffusion Barriers Between Al and Cu for the Cu Interconnect of Memory Devices

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We report a comparative study on the diffusion barrier performance of transition metal nitride thin films, including TiN_x, TaN_x, and WN_x, between Al and Cu deposited by ionized physical vapor deposition (IPVD) or atomic layer deposition (ALD), which is particularly important for the integration of the Cu interconnect into memory devices such as dynamic random access memory and NAND Flash. Without a suitable diffusion barrier, various kinds of Al–Cu intermetallic compounds were formed, even after annealing at 200°C for 30 min. Sheet resistance measurements, X-ray diffractometry, and cross-sectional view transmission electron microscopy analysis combined with energy-dispersive spectroscopy consistently showed that the insertion of a 10-nm-thick IPVD-TiN_x or IPVD-TaN_x layer between the two layers retarded the interdiffusion of Al and Cu during the annealing at 400 or 450°C, respectively, for 30 min in a high vacuum ($<5 \times 10^{-5}$ Torr). Noticeably, ALD-WN_x prepared using a sequential supply of B_2H_6, WF_6, and NH_3, could effectively prevent the interdiffusion of Al and Cu and the formation of Al–Cu intermetallic compounds up to an annealing temperature of 550°C for 30 min.

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Cu metallizations in logic devices have been extensively studied for more than 20 years, and the integration of Cu interconnects into commercial logic devices has been successfully achieved. However, little work has been done on the evaluation of their validity in memory devices such as dynamic random access memory and NAND Flash. This is an emerging but important area technologically and scientifically, as the performance level should meet the stringent requirements for high-bandwidth, high-speed, and high-density memory devices. A conventional Cu wiring technology integrated into logic devices, such as a Ta/TaN diffusion barrier and Cu seed layer deposited by ionized physical vapor deposition (IPVD) and via/trench filling of Cu by electroplating, followed by chemical mechanical polishing, could also be used for memory devices. For more information, the reader can refer to some excellent papers related to Cu wiring technology for logic devices.[1-3]

However, a different interconnect scheme can be applied when the Cu interconnect is integrated into memory devices. This is because the fabrication of memory devices requires a more cost-effective solution as compared to that of logic devices. One of the promising options for the interconnect structure in memory devices is to use a Cu interconnect with an Al interconnect. For example, the Cu interconnect, which is formed by a single damascene process, is used as a bit line or the first-level metal, while Al is used for contact filling and the second-level metal line. Many companies that produce memory devices already have a lot of physical vapor deposited (PVD) Al chambers and reflow chambers, which have been used to fabricate the metal 2/metal 2 contact (or via) and metal 3/metal 3 contact (or via). Moreover, because the Al via and Al line can be simultaneously fabricated by Al deposition and Al reflow after via and trench formation by the dual damascene process, the fabrication cost can be more reduced. Al interconnect can still be used as a fuse line to repair redundancy cells in order to improve the yield or pad line, although Cu interconnect is adopted in memory devices. In these cases, some contact between Al and Cu is inevitable. Here, the Al reflow process to be used for the simultaneous formation of Al via and Al line is generally performed at more than 500°C.[4,5] This can lead to reliability issues concerning the interconnect scheme, such as an unwanted increase of the interconnect resistance or morphological change of the interconnect structure, such as void formation, because the Al–Cu binary phase diagram predicts the formation of intermetallic compounds at temperatures as low as 300°C.[6] In order to solve these problems, a suitable diffusion barrier should be inserted between Al and Cu.

The first approach to find a suitable diffusion barrier between Al and Cu is to test the well-known materials employed as a diffusion barrier for Cu or Al interconnects and to confirm the possibility of extending their applications to Cu-based interconnects for memory devices. Various materials have been investigated as a diffusion barrier for Cu metallizations, including refractory metals (Ti, W, Ta, Zr, Mo, etc.), their nitrides (TiN, TaN, Ta_2N, W_2N, etc.), silicides ($TiSi_2$, $TaSi_2$, etc.), and ternary alloys (Ta–Si–N, Ti–Si–N, W–Si–N, etc.).[7] Among them, transition metal nitrides such as Ti, Ta, W nitrides have been the most widely studied because of their high melting temperatures, relatively low resistivities, and thermodynamic stability for Cu. Thus, we selected TiN_x, TaN_x, and WN_x as candidates for diffusion barrier materials between Al and Cu in this study. Here, TaN_x has been typically used for the Cu-based metallizations of logic devices, while TiN_x is used as a diffusion barrier for Al-based ones. WN_x can be one of the candidates because WN_x films have frequently been reported to form an amorphous phase, unlike Ti–N and Ta–N systems, which possess a desirable structure as diffusion barriers.[8]

In order to evaluate the barrier performances between Al and Cu, structures consisting of Al (100 nm)/diffusion barriers (10 nm)/Cu (90 nm)/Ta (5 nm) were prepared on SiO_2 (100 nm)/Si substrates (Fig. 1). A Ta layer deposited on SiO_2 was used to improve the adhesion of Cu on SiO_2. Then, transition nitride thin films, such as TiN_x, TaN_x, and WN_x, were deposited as diffusion barriers. Table I summarizes the details for the diffusion barriers evaluated in this study. We also evaluated the performances of the material prepared by atomic layer deposition (ALD) for interconnect scaling, which can provide excellent step coverage, while both TiN_x and TaN_x were deposited by IPVD. In this study, we focus on the ALD-WN_x film, which was deposited using WF_6, NH_3, and B_2H_6 at 300°C. The detailed deposition conditions for ALD-WN_x are reported elsewhere.[9] Then, these multilayer structures were annealed in a high vacuum ($<5 \times 10^{-5}$ Torr) for 30 min at temperatures ranging from 350 to 550°C with intervals of 50°C. The barrier performances were evaluated using various analysis tools after annealing, viz. sheet resistance measurements using a conventional four-point probe, X-ray diffractometry (XRD), and transmission electron microscopy (TEM, JEOL JEM-3000F with a field emission gun oper-

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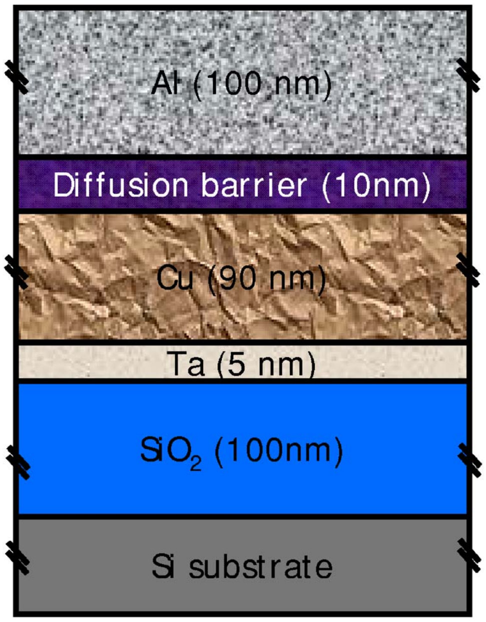

Figure 1. (Color online) A sample structure prepared in this study to test the performance of diffusion barriers between Al and Cu.

ated at 300 kV). We also used energy-dispersive spectroscopy (EDS) analysis in scanning TEM mode to characterize the interdiffusion of Al and Cu through the diffusion barriers and possible formation of intermetallic compounds.

Figure 2a shows the XRD results of the Al/Cu multilayer structure without a diffusion barrier. Even after annealing at 200°C for 30 min in a high vacuum ($<5 \times 10^{-5}$ Torr), intermetallic compounds including stoichiometric AlCu, as well as Cu-rich and Al-rich ones, were formed, as expected from the Al–Cu binary phase diagram, resulting in an increase of the resistance of this metallization scheme. The dominant Al–Cu intermetallic compounds are AlCu and Al_2Cu, which is the same result as that previously obtained for friction-welded Cu/Al bimetallic joints.[10] In order to solve this problem, diffusion barriers were inserted between Al and Cu.

First, the diffusion barrier properties between Al and Cu were evaluated by sheet resistance measurements after annealing (Fig. 2b). There is scarcely any change in the sheet resistance of the film up to an annealing temperature of 400°C for 30 min in a high vacuum ($<5 \times 10^{-5}$ Torr) for all of the samples. This means that by inserting the diffusion barriers, the initial state of the multilayer structure consisting of Al/diffusion barrier/Cu is preserved or the reaction between Al and Cu is prevented until an annealing temperature of 400°C is reached. In the case of the IPVD-TiN_x diffusion barrier, the sheet resistance starts to increase after annealing at 450°C, which indicates the possible interdiffusion of Al and Cu through the diffusion barrier or interfacial reactions. The sheet resistance considerably increases when the annealing temperature is further increased to 500°C. In the case of IPVD-TaN_x, the initial increase in the sheet resistance is observed after annealing at 500°C, which is 50°C higher than that in the Al/IPVD-TiN_x/Cu sample, and the sheet resistance continuously increases as the annealing temperature is further increased to 550°C. However, for the Al/ALD-WN_x/Cu structure, no increase in the sheet resistance is observed, even after annealing at 550°C.

Table I. Summary of diffusion barriers investigated in this study.

Materials	Resistivity ($\mu\Omega$ cm)	Density[a] (g/cm^3)	Metal/N ratio in the film	Deposition note
TiN_x	200	4.9	1	IPVD
TaN_x	220	15.1	1.1	IPVD
WN_x	350	15.1	1.2	ALD with precursors of WF_6, NH_3, and B_2H_6. Deposition temp.: 300°C

[a] Film density was determined by X-ray reflectance.

Figures 2c and d show the XRD results of the multilayer structures with diffusion barriers between Al and Cu with annealing. In the Al/IPVD-TiN_x/Cu structure, the formation of Al–Cu intermetallic compounds started to be observed after annealing at 450°C for 30 min in a high vacuum ($<5 \times 10^{-5}$ Torr), although the intensity is very low (not shown here). In the case of the Al/IPVD-TaN_x/Cu structure (Fig. 2c), Al–Cu intermetallic compounds start to be detected after annealing at 500°C, which is the same temperature as that where the sheet resistance starts to increase. As the annealing temperature is increased to 550°C, the intensities of the peaks from Al–Cu intermetallic compounds increase, which explains the considerable increase in the sheet resistance of the multilayer structure, as shown at Fig. 2b. When ALD-WN_x is used as a diffusion barrier, the formation of Al–Cu intermetallic compounds is not observed, even after annealing at 550°C (Fig. 2d), suggesting that ALD-WN_x effectively prevents the interdiffusion of Cu and Al through it. It is quite interesting to note that, in the case of all of the Al/diffusion barrier/Cu structures, the annealing temperatures at which the formation of Al–Cu intermetallic compounds starts to be observed by XRD are the same as the temperatures at which the sheet resistance starts to increase. This indicates that the increase in the sheet resistance discussed in the previous paragraph is mainly caused by the formation of Al–Cu intermetallic compounds, which have much higher resistivities than Al and Cu.[10,11]

In order to confirm the interdiffusion of Al and Cu through the diffusion barrier or possible interfacial reactions, TEM analysis combined with EDS was performed. Figures 3a and b show the cross-sectional view TEM (XTEM) images of the as-deposited and 500°C-annealed Al/IPVD-TaN_x/Cu stacks. From the as-deposited image, the interfaces of the multilayer structure are clearly observed and no reaction between Al and Cu is shown. The XTEM image of the sample annealed at 500°C for 30 min in a high vacuum ($<5 \times 10^{-5}$ Torr) also shows that the multilayer structure seems to be preserved. However, a careful investigation of the TEM image shows that the microstructures of the original Cu and Al are significantly changed, although they are difficult to exactly characterize. However, the corresponding EDS analysis clearly confirms the interdiffusion of Al and Cu (Fig. 3d). One can observe the Al peak at the initial location of the Cu layer and vice versa. The composition at the initial location of Al (top of the multilayer) was determined to be ~37 atom % Cu and ~63 atom % Al after annealing at 500°C. This is close to the stoichiometry of Al_2Cu, which is consistent with the XRD results showing that the dominant compound formed is θ-Al_2Cu phase. Interestingly, the composition at the initial location of Cu (bottom of the multilayer) was determined to be ~11 atom % Al and ~89 atom % Cu, suggesting that the fast diffusing species is Cu. For comparison, the EDS spectra of the sample annealed at 450°C was obtained (Fig. 3c), which showed no noticeable change as compared with that obtained before annealing, indicating that the IPVD-TaN_x effectively prevented the interdiffusion of Cu and Al. Figures 4a and b show the XTEM images of the as-deposited and 550°C-annealed Al/ALD-WN_x/Cu stack. One cannot observe any difference in the XTEM images of the two samples. The multilayer structure seems to be intact, even after annealing at 550°C, and the interfaces are preserved. In fact, no change in the EDS spectra is observed after annealing, indicating that the ALD-WN_x layer effectively prevented the interdiffusion of Cu and Al through it (Fig. 4c).

This study shows that the interdiffusion and reaction between Al and Cu is retarded by inserting very thin transition metal nitride thin

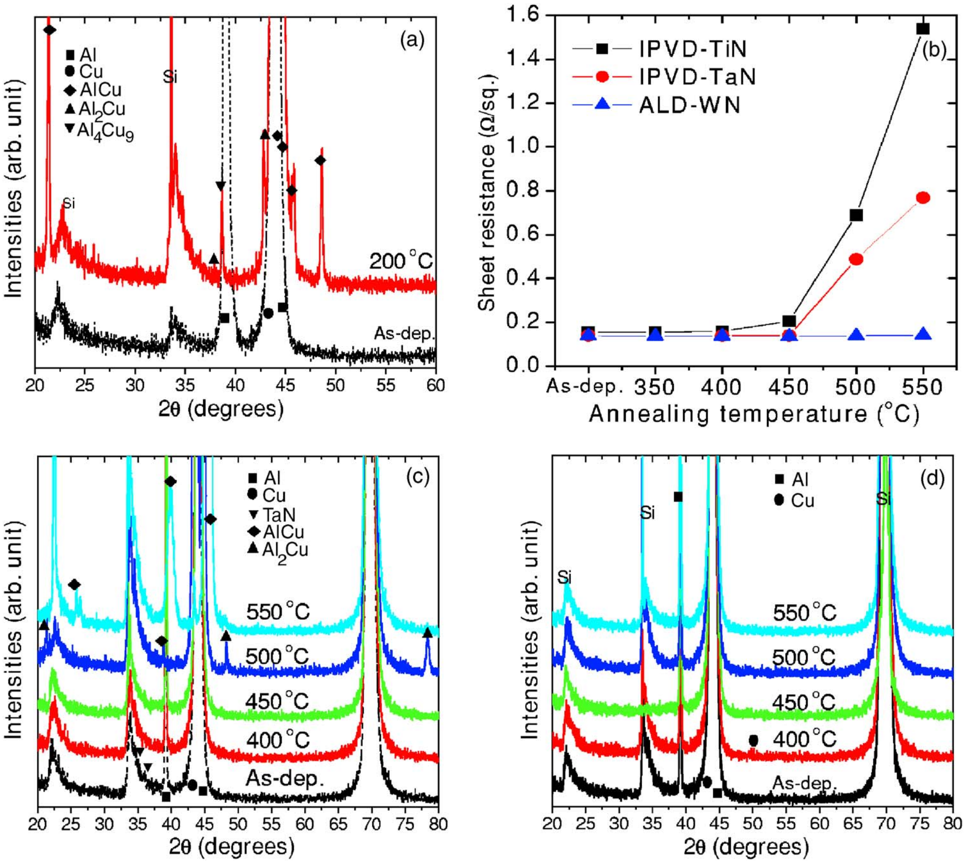

Figure 2. (Color online) (a) XRD results of Al/Cu multilayer without a diffusion barrier between Al and Cu. (b) Change in the sheet resistance of the multilayer structure with diffusion barriers shown in Fig. 1 as a function of the annealing temperature. XRD results of (c) Al/IPVD-TaN_x/Cu structure and (d) Al/ALD-WN_x/Cu structure at various annealing temperatures. Annealing was performed in a high vacuum ($<5 \times 10^{-5}$ Torr) during 30 min.

films such as TiN_x, TaN_x, and WN_x. However, the abilities of these films to prevent the interdiffusion of Al and Cu through the diffusion barrier were significantly different from each other, with TiN_x being the worst and WN_x the best. Generally, the performance of the diffusion barrier is mainly determined by its microstructure or density.[7,12,13] The polycrystalline microstructure of TiN_x with its columnar grains explains its relatively poor barrier performance. The thermodynamical instability of the Al/TiN interface, leading to the formation of a Ti–Al reaction layer at low temperature, may be another reason.[14] In the case of ALD-WN_x, the specific XRD peaks

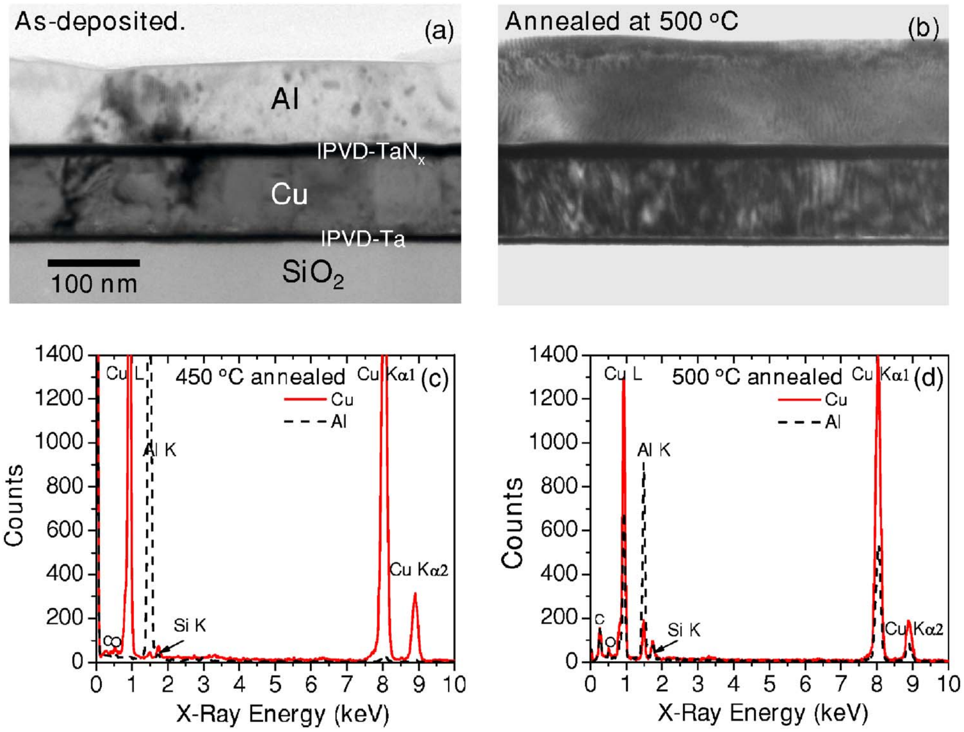

Figure 3. (Color online) XTEM images of Al/IPVD-TaN_x/Cu (a) as-deposited and (b) annealed at 500°C. (c) EDS spectra of the same samples obtained at the initial locations of the Cu and Al layers after annealing at (c) 450 and (d) 500°C, respectively.

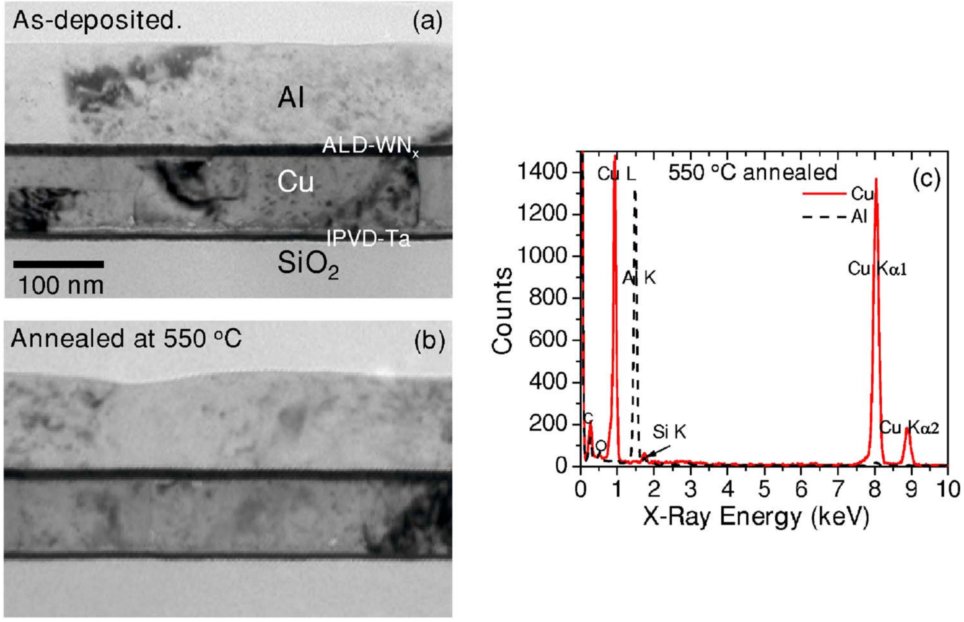

Figure 4. (Color online) XTEM images of Al/ALD-WN$_x$/Cu (a) as-deposited and (b) annealed at 550°C. (c) EDS spectra of the sample after annealing at 550°C obtained at the initial locations of the Cu and Al layers.

from hexagonal WN or cubic β-W_2N are hardly observed (see Fig. 2d), indicating that the ALD-WN$_x$ layer has a structure which is close to amorphous. In fact, a high-resolution XTEM image showed that the ALD-WN$_x$ film deposited using B_2H_6, WF_6, and NH_3 formed nanocrystals a few nanometers in size.[15] It was also reported that the ALD-WN$_x$ film had a high density of approximately 15 g/cm^3.[9] Thus, the formation of a dense nanocrystalline microstructure close to amorphous might explain its superior diffusion barrier performance.

In summary, we investigated the diffusion barrier performances of transition metal nitride thin films, viz. IPVD-TiN$_x$, IPVD-TaN$_x$, and ALD-WN$_x$, between Al and Cu for the implementation of Cu interconnects in memory devices. The results emphasize the need for a suitable barrier material and the development of the corresponding process for the successful integration of Cu interconnects in memory devices. From the results, it can be concluded that ALD-WN$_x$ deposited using WF_6, B_2H_6, and NH_3 can be a viable candidate diffusion barrier between Al and Cu. ALD-WN$_x$, with a thickness of 10 nm, effectively prevented the interdiffusion of Al and Cu until annealing at a temperature of 550°C in a high vacuum ($<5 \times 10^{-5}$ Torr) was reached. The TEM/EDS analysis indicated that the failure mechanism of the diffusion barriers between Al and Cu was closely related to the thermodynamical stability of the multilayer structures and the microstructure of the diffusion barriers, which will be discussed in a separate paper.[14] We hope that this study will inspire extensive relevant studies for a successful integration of the simultaneous use of Cu and Al interconnects for future memory devices. For example, we think that an evaluation of the performances of many other ultrathin ALD diffusion barriers (<5 nm) is critically needed for continuously shrinking memory devices, as shown by the International Technology Roadmap for Semiconductors.[16]

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References

1. D. Edelstein, C. Uzoh, C. Cabral, Jr., P. DeHaven, P. Buchwalter, A. Simon, E. Cooney III, S. Malhotra, D. Klaus, H. Rathore, B. Agarwala, and D. Bguyen, in *Advanced Metallization Conference in 2001*, A. J. McKerrow, Y. Shacham-Diamond, S. Zaima, and T. Ohba, Editors, Warrendale, PA, *Mater. Res. Soc. Proc.*, p. 541 (2002).
2. J. Reid, *Jpn. J. Appl. Phys.*, **40**, 2650 (2001).
3. K. Maex, M. R. Baklanov, D. Shamiryan, F. Lacopi, S. H. Brongersma, and Z. S. Yanovitskaya, *J. Appl. Phys.*, **93**, 8793 (2003).
4. K.-I. Choi, S.-H. Han, S. Yun, D.-Y. Kim, J. W. Hong, S. W. Lee, B. H. Kim, S.-T. Kim, U.-I. Chung, J.-T. Moon, and B.-I. Ryu, *Jpn. J. Appl. Phys.*, **45**, 2987 (2006).
5. C.-H. Kim, S.-W. Lim, H.-P. Kim, I.-C. Ryu, B.-S. Eun, S.-H. Kim, I.-C. Rho, Y.-S. Sohn, H.-S. Kang, and H.-J. Kim, in *Proceedings of the IEEE International Interconnect Technology Conference 2007*, IEEE, p. 43 (2007).
6. *Binary Alloy Phase Diagrams*, Vol. 1, T. B. Massalski, Editor, p. 142, ASM International, Materials Park, OH (1990).
7. A. E. Kaloyeros and E. Eisenbraun, *Annu. Rev. Mater. Sci.*, **30**, 363 (2000).
8. M. Uekubo, T. Oku, K. Nii, M. Murakami, K. Takahiro, S. Yamaguchi, T. Nakano, and T. Ohta, *Thin Solid Films*, **286**, 170 (1996).
9. S.-H. Kim, J.-K. Kim, N. Kwak, H. Sohn, J. Kim, S.-H. Jung, M.-R. Hong, S. H. Lee, and J. Collins, *Electrochem. Solid-State Lett.*, **9**, C54 (2006).
10. W.-B. Lee, K.-S. Bang, and S.-B. Jung, *J. Alloys Compd.*, **390**, 212 (2005).
11. M. Abbasi, A. K. Taheri, and M. T. Salehi, *J. Alloys Compd.* **319**, 233 (2001).
12. H. Kattelus and M.-A. Nicolet, in *Diffusion Phenomena in Thin Films and Microelectronics Materials*, D. Gupta and P. S. Ho, Editors, pp. 432–498, Noyes Publications, Park Ridge, NJ (1988).
13. K.-C. Park, K.-B. Kim, I. Raaijmakers, and K. Ngan, *J. Appl. Phys.*, **80**, 5674 (1996).
14. S.-H. Kim, D.-J. Lee, S.-S. Yim, H.-M. Kim, K.-S. Kim, K.-B. Kim, and H. Sohn, In preparation.
15. S.-H. Kim, J.-K. Kim, J. H. Lee, N. Kwak, J. Kim, S.-H. Jung, M.-R. Hong, S. H. Lee, J. Collins, and H. Sohn, *J. Electrochem. Soc.*, **154**, D435 (2007).
16. http://www.itrs.net/Links/2006Update/FinalToPost/09_Interconnect2006Update.pdf (March 6, 2008).