

Comparative Study of Annealing Effects on the Structural Properties of TiN and TiAlN Coatings

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In a comparative study of the influence of thermal annealing processes on TiN and TiAlN coatings prepared by DC magnetron sputtering, we characterized the samples by using x-ray diffraction and scanning electron microscopy. The annealing temperature significantly affected the structural properties of the coatings. The TiO₂ phase was generated in the TiAlN coatings by thermal annealing at a higher temperature than in the TiN coatings.

Keywords: TiN, TiAlN, annealing, coatings

1. INTRODUCTION

Titanium nitride (TiN) coatings have been used in a variety of applications due to their exceptional physical and chemical properties, such as wear resistance, corrosion resistance, chemical stability, and a diffusion barrier property. When applied to machining tools and engineering components, the coatings are subjected to particularly demanding work conditions,^[1-4] such as elevated temperatures and an oxidizing atmosphere. Furthermore, when used as diffusion barrier layers in the manufacture of state-of-the-art integrated circuits (ICs),^[5,6] these materials may encounter problems because of the use of oxygen-containing ambients in the IC processing.

Accordingly, the need to improve the oxidation resistance of TiN coatings has induced a greater effort to develop the ternary compounds of (Ti, X) N. The new coating material TiAlN^[7] has attracted considerable attention because it has a much better wear resistance and a longer tool life than the TiN coatings. Several researchers have used thermal annealing to investigate the oxidation properties of TiAlN.^[8-11] Although thermal annealing significantly changes the structural properties of the coatings, only a few reports directly compare TiN and TiAlN coatings with respect to their microstructures; Kim et al., for instance, compared annealed TiN and TiAlN films prepared by plasma-assisted chemical vapor deposition.^[12]

In this research, we compare the annealing effects on TiN and TiAlN coatings prepared by sputtering, particularly in

terms of microstructural changes under various annealing temperatures. We investigated the three-dimensional film morphology by using plan-view and cross-sectional scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. EXPERIMENT

First, we formed a 100 nm layer of thermal oxide on Si (100) wafers. On this layer, we deposited a 200 nm layer of TiN or TiAlN by using a DC magnetron sputtering machine with a Ti and Ti/Al target, respectively, in an Ar/N₂ atmosphere. For the deposition of TiN, we used a substrate temperature of 100°C, a DC power level of 20 kW, and a pressure level of 4 mTorr. For the deposition of TiAlN, we used a substrate temperature of 25°C, a DC power level of 3 kW, and a pressure level of 5 mTorr. The average compositions of the coatings were Ti_{0.50}N_{0.50} and Ti_{0.35}Al_{0.15}N_{0.50}.

After the deposition, the samples were annealed in a quartz tube furnace at temperatures of 500°C, 750°C and 1000°C in an Ar ambient for 1 h. The flow rate of the Ar gas was set at 0.5 slm. To analyze the structural characteristics of the coatings, we used SEM (Hitachi S-4200) and grazing angle XRD (Philips, CM20T, 200 kV) with an incident angle of 0.5° and CuKα₁ radiation ($\lambda = 0.154056$ nm).

3. RESULTS AND DISCUSSION

To investigate the effect of thermal annealing on the crystallinity of thin coatings, we performed a grazing angle XRD analysis. Figure 1 shows XRD patterns of as-deposited and heat-treated TiN coatings. As for the as-deposited TiN coatings and the 500°C-annealed TiN coatings (Figs. 1(a) and

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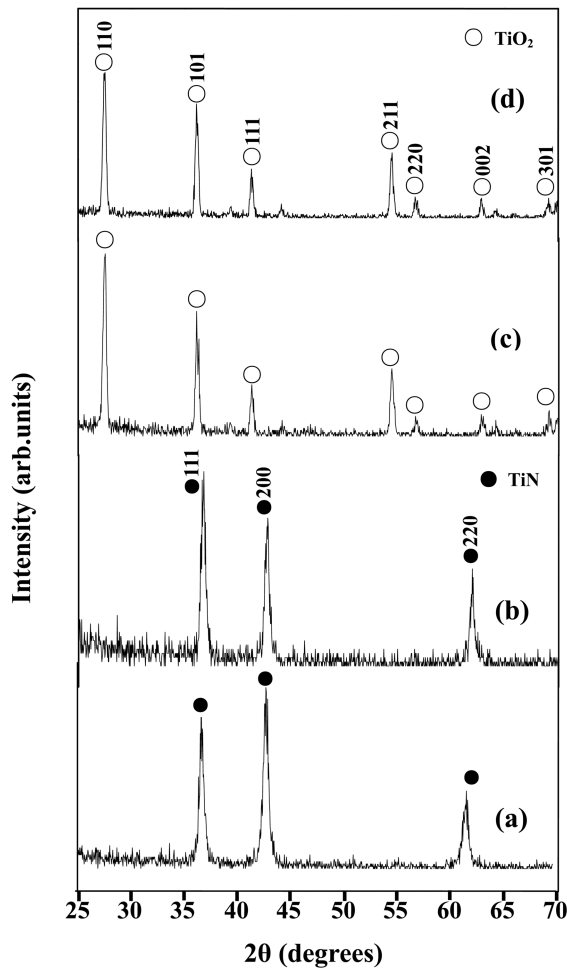


Fig. 1. XRD patterns of the (a) as-deposited, (b) 500°C-annealed, (c) 750°C-annealed, and (d) 1000°C-annealed TiN thin film coatings.

1(b)), the lines observed in the diffractogram coincide with the (111), (200) and (220) peaks of the TiN (JCPDS 38-1420). In the case of 750°C and 1000°C-annealed TiN coatings, no TiN-related peaks observed and showing only TiO₂ peaks (JCPDS 21-1276).^[12] The existence of the TiO₂ peaks results from the oxidation of the TiN coatings. Figure 2 shows XRD patterns of the as-deposited and heat-treated TiAlN coatings. The as-deposited and 750°C-annealed samples show the diffraction peaks that correspond to the TiAlN crystal. Note that the TiAlN peaks in Fig. 2 shift to a higher 2θ value than the TiN peaks shown in Fig. 1; this difference is due to the shrinkage that occurs in the lattice parameter as some of the Ti atoms are replaced with Al atoms. In the case of the TiAlN coatings, the peaks that correspond to any of the titanium oxide crystallites were not clearly observable even after heat treatment at 750°C; this outcome contrasts with the case of the TiN coatings. We deduce therefore that TiAlN in this annealing route has a better anti-oxidation property than TiN up to 750°C. The 1000°C-annealed TiAlN coatings had diffraction peaks corresponding to the tetrago-

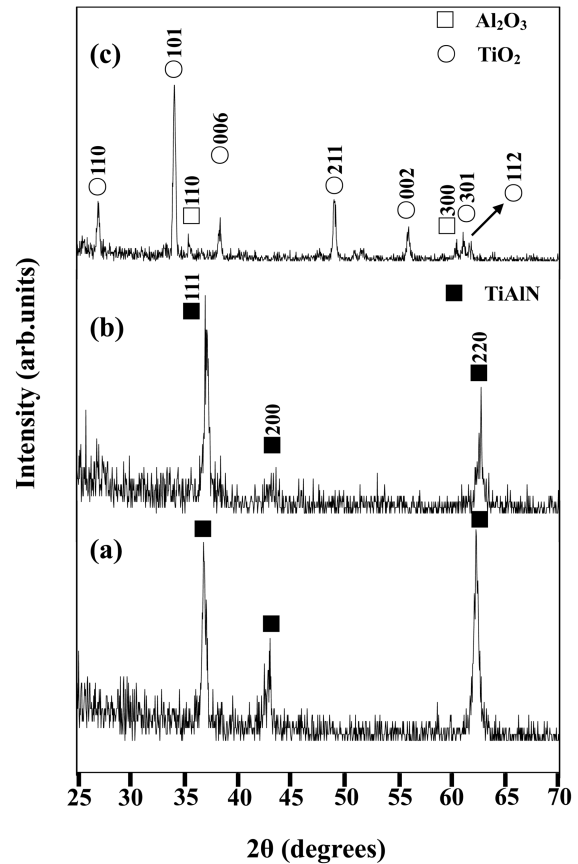


Fig. 2. XRD patterns of the (a) as-deposited, (b) 750°C-annealed, and (c) 1000°C-annealed TiAlN thin film coatings.

nal rutile TiO₂ structure with some weak Al₂O₃ peaks.

Figures 3(a), 3(b), 3(c), and 3(d) show cross-sectional SEM images of as-deposited, 500°C-annealed, 750°C-annealed and 1000°C-annealed TiN thin coatings, respectively. The insets represent the corresponding plan-view images. The as-deposited and 500°C-annealed samples exhibited smooth surface morphologies, though a pronounced and well-developed grain structure appeared in the coatings after thermal annealing at 750°C and 1000°C, causing the surfaces to become rough. Figure 4 shows cross-sectional and plan-view (inset) SEM images of the TiAlN thin coatings. The images indicate that clusters of large grain-like structures are observable in the coatings after thermal annealing at 1000°C but not in the as-deposited, 500°C-annealed and 750°C-annealed samples.

By comparing the SEM images with the XRD data, we can surmise that the large grain-like structures are mainly caused by the nucleation and growth of the rutile TiO₂ crystallites identified in the XRD patterns. We deduce that the oxygen in the TiO₂ originates from the air leakage or the residual oxygen in the furnace. Additionally, although we flowed Ar gas during the oxidation, commercially available Ar gas usually contains a small amount of oxygen, which, at

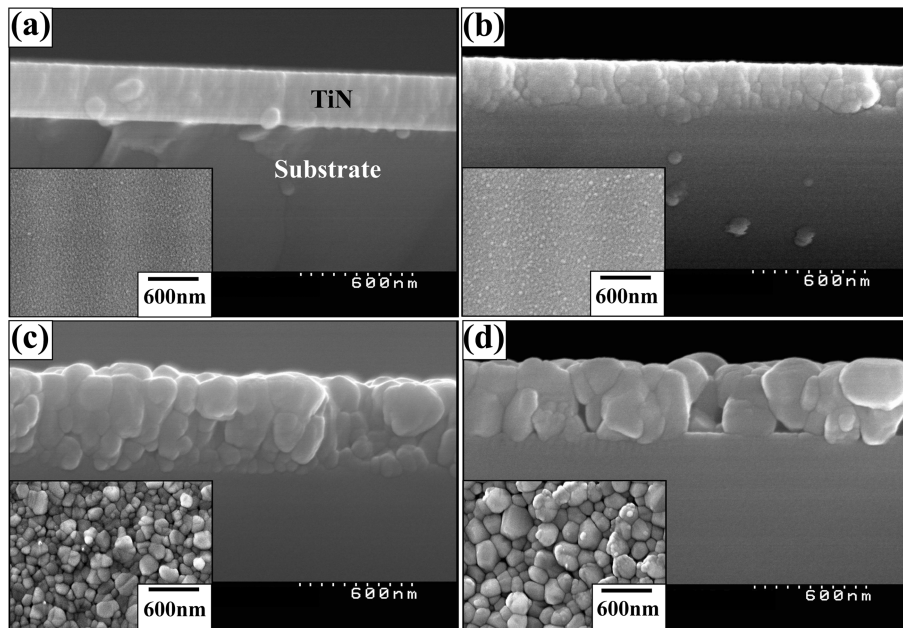


Fig. 3. Cross-sectional SEM images of (a) as-deposited, (b) 500°C-annealed, (c) 750°C-annealed, and (d) 1000°C-annealed TiN thin film coatings.

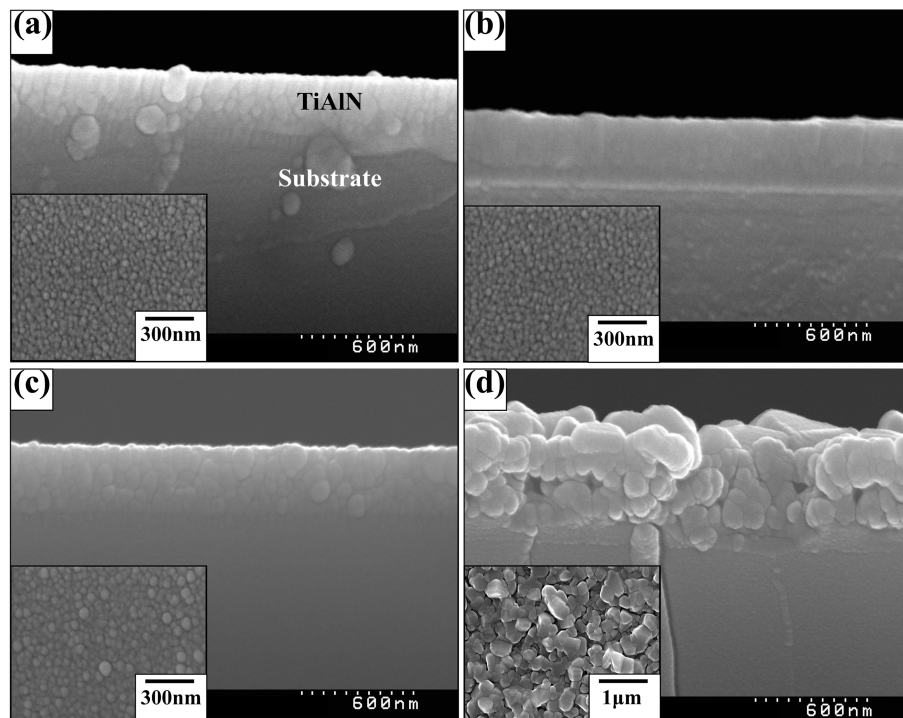


Fig. 4. Cross-sectional SEM images of (a) as-deposited, (b) 500°C-annealed, (c) 750°C-annealed, and (d) 1000°C-annealed TiAlN thin film coatings.

high temperature, is enough to oxidize many materials such as TiN and TiAlN.^[13] The cross-sectional SEM image indicates that the thicknesses of the coatings significantly increase whenever TiN or TiAlN changes into TiO₂. This change in the thickness of the samples is mainly due to the increase in volume during the oxidation. Furthermore, as

shown in Figs. 3(d) and 4(d), the increase in volume may induce stress between the layers, resulting in the formation of cracks.

The oxidation resistance of TiAlN is reportedly due mainly to Al. The Al forms an amorphous aluminum oxide surface layer, which hinders the diffusion of oxygen through

the film. On the basis of the XRD pattern shown in Fig. 2(b), we also deduce that the aluminum oxide layer that forms on the 750°C-annealed TiAlN coatings is not crystalline. Further investigation is currently underway.^[14-19]

4. CONCLUSIONS

In summary, we compared the annealing behavior of TiN and TiAlN coatings prepared by a DC magnetron sputtering method. XRD analysis shows that a TiO₂ rutile phase is present at higher annealing temperatures. Our analysis also reveals that TiAlN has superior anti-oxidation properties up to 750°C, whereas pure TiN tends to oxidize at temperatures greater than 750°C. SEM images indicate that thermal annealing leads to relatively well-developed grains that correspond mainly to the TiO₂ rutile structure. The coating with the TiO₂ structure is thicker than the coatings without the TiO₂ structure.

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REFERENCES

1. W.-B. Im, Y.-H. Won, Y.-I. Kim, H.-S. Jang, and D.-Y. Jeon, *Electron. Mater. Lett.* **2**, 1 (2006).
2. S. Yoo, *Electron. Mater. Lett.* **3**, 195 (2006).
3. M. J. Lee and Y. S. Kim, *Electron. Mater. Lett.* **3**, 155 (2007).
4. I.-S. Park, K.-R. Kim, Y.-S. Kim, and J. Ahn, *Electron. Mater. Lett.* **2**, 107 (2006).
5. J. Ahopelto, H. P. Kattelus, J. Saarilahti, and I. Suni, *J. Crystal Growth* **99**, 550 (1990).
6. S. Nagasawa, K. Hinode, T. Satoh, H. Akaike, Y. Kitagawa, and M. Hidaka, *Physica C* **412-414**, 1429 (2004).
7. Y. Tanaka, T. M. Gür, M. Kelly, S. B. Hagstrom, T. Ikeda, K. Wakihara, and H. Satoh, *J. Vac. Sci. Technol. A* **10**, 1749 (1992).
8. D. McIntyre, J. E. Greene, G. Hakansson, J. E. Sundgren, and W. D. Münz, *J. Appl. Phys.* **67**, 1542 (1990).
9. P. Panjan, B. Navinsek, M. Cekada, and A. Zalar, *Vacuum* **53**, 127 (1999).
10. Q. G. Zhou, X. D. Bai, X. Y. Xue, X. W. Chen, J. Xu, and D. R. Wang, *Surf. Coat. Technol.* **191**, 212 (2005).
11. B. Y. Man, L. Guzman, A. Miotello, and M. Adami, *Surf. Coat. Technol.* **180-181**, 9 (2004).
12. C.-W. Kim and K. H. Kim, *Thin Solid Films* **307**, 113 (1997).
13. F. H. Lu and H. Y. Chen, *Thin Solid Films* **355-356**, 374 (1999).
14. Y.-H. Kim, *Electron. Mater. Lett.* **2**, 31 (2006).
15. S.-J. Hong and J.-I. Han, *Electron. Mater. Lett.* **2**, 131 (2006).
16. J.-G. Lee, C. Kim, B. Kim, D. Son, and B. Park, *Electron. Mater. Lett.* **2**, 111 (2006).
17. T.-K. Lee, F. Hua, and J. W. Morris, Jr., *Electron. Mater. Lett.* **2**, 157 (2006).
18. J.-H. Noh, S.-H. Lee, S. Lee, and H.-S. Jung, *Electron. Mater. Lett.* **4**, 71 (2008).
19. M.-J. Kim and J.-B. Yoo, *Electron. Mater. Lett.* **4**, 59 (2008).