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Characterization of DC magnetron sputtering deposited thin films of TiN for SBN/MgO/TiN/Si structural waveguide*

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Abstract: Optimal parameters for depositing Titanium nitride (TiN) thin films by DC reactive magnetron sputtering were determined. TiN thin films were deposited on Si (100) substrates by DC reactive magnetron sputtering, at different temperatures, different electrical current values, and different N_2/Ar ratios. Structural characteristics of TiN thin films were measured by X-ray diffraction (XRD); surface morphology of the thin films was characterized using an atomic force microscope (AFM). The electric resistivity of the TiN films was measured by a four-point probe. In the result, temperature is 500 °C, electrical current value is 1.6 A, pure N_2 is the reacting gas, TiN thin film has the preferred (200) orientation, resistance is small enough for its use as bottom electrodes.

Key words: Titanium nitride (TiN), Thin film, Sputtering, Orientation, Waveguide
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INTRODUCTION

Monocrystalline SBN (Strontium barium niobium, $Sr_xBa_{1-x}Nb_2O_6$, denoted SBNx·100, where $0.25\leq x\leq 0.75$) solid solution, is currently being investigated as potential material for many micro-device applications, such as piezoelectric infrared detectors, piezoelectric, electro-optic modulators, and holographic storage (Koch *et al*., 1998), because SBN has one of the largest known linear electro-optic coefficients (r_{33}=1300 pm/V for SBN75), two orders of magnitude larger than that of the primary electro-optic material $LiNbO_3$ (Cuniot-Ponsard *et al*., 2003), the industry standard. Thanks to rapid development of the integrated circuit (IC) industry, it is possible to investigate optical waveguide based on Si. However, realization of the excellent electro-optic properties of SBN requires successful heteroepitaxial growth of the (001) SBN film in direction perpendicular to the lattice-matched substrate plane, because the mismatches between SBN and Si substrate are $M_a=M_b$=12.6%, M_c=37.1%.

Titanium nitride (TiN) is a rocksalt-structure (NaCl structure) compound consisting of Ti atoms filled in FCC-based lattice with all octahedral sites filled with nitrogen atoms (Fig.1). Physical properties are: Lattice parameter: 0.424 nm; Melting point: 2900 °C; Thermal stability (ΔH^{298}): 336.6 kJ/mol; Young's modulus: 450 GPa. TiN thin films have been used for various applications, such as decorative coatings, hard coatings, wear-resistant coatings and diffusion barrier in IC technology. We developed a multilayer structure as SBN/MgO/TiN/Si. TiN thin films were used as buffer layer, bottom electrodes, and diffusion barrier. The lattice constant of MgO (0.4213 nm) is close to that of TiN (0.424 nm) and SBN. It has been shown that the MgO thin films used as buffer layer between the semiconductor and the oxide material, such as a high T_c superconductor and a ferroelectric material, will lead to better results than the deposition

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of oxide material directly onto the semiconductor substrates. On the other hand, the refractive index of MgO is 1.73, so it can form the above waveguide structure. Whereas the lattice constant of Si (100) is 0.543 nm, TiN suites to it well because 0.543×3≈ 0.424×4.

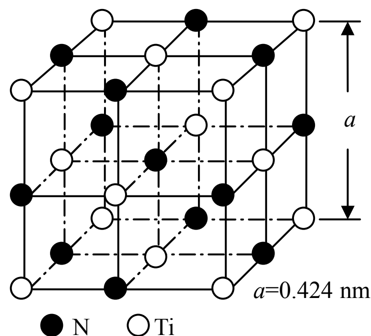

Fig.1 Schematic structure of TiN

Researches on thin films based on TiN have been carried out for many years. Many studies have been conducted to investigate the relationships between the deposition parameters and film structure (Huang *et al*., 1999; Groudeva-Zotova *et al*., 2000; Chou *et al*., 2001; Chen *et al*., 2001; Sundgren, 1985). Reported film preparation results showed that different deposition systems had different effects on TiN films structure (Kelly and Armell, 2000; Huang *et al*., 2000). The initial growth and texture formation mechanism of TiN films were investigated by using reactive magnetron sputtering of a Ti metallic target to deposit the TiN films on (111) silicon substrates under an N_2/Ar atmosphere (Li *et al*., 2002). The reactive magnetron sputtering method has become popular for coating industry, because the coating products have high hardness, good chemical stoichiometry and the target is without physical confining (Sundgren, 1985; Arnell *et al*., 1996).

In this work, we analyzed TiN thin films deposited at different substrate temperatures, different electrical current values, and different N_2/Ar ratios by DC reactive magnetron sputtering with X-ray diffraction (XRD), atomic force microscope (AFM), and four-point probe. Optimal parameters for deposition of TiN thin films were achieved.

EXPERIMENTS

TiN thin films were deposited by DC reactive magnetron sputtering on Si (100) substrates at different N_2/Ar ratios, temperatures, and electrical current values. The distance between substrate and target is 100 mm, the diameter and thickness of Ti metallic target is 60 mm and 5 mm, respectively. The purity of Ti is 99.99% and that of N_2 and Ar is 99.999%. The substrate is Si (100) and the total flow of argon and nitrogen was set to be 80 sccm. Prior to all depositions, the titanium target was pre-cleaned in pure argon for 5 min to remove the oxide layer from the target. The structural characteristics of the TiN thin films were measured by X-ray diffraction (XRD) (CuKα, Philip, PW3710). Surface morphology of the thin films was characterized by an atomic force microscope (Seiko, SPI3800A, AFM). The electric resistivity of the TiN thin films was measured by a four-point probe (semiconductor material graduate school in Guangzhou, China, SDY-4).

RESULTS

X-ray diffraction analysis

X-ray diffraction measurements were conducted with a Philip, PW3710 diffract-meter equipped with a diffracted-beam monochromatic set to select the Cu Ka radiation (Figs.2~4).

As Fig.2 shows, when Ar-content in the sputtering gas mixtures was more (Fig.2a, N_2:Ar=1:9), TiN thin film was (111) orientated basically, the (200) orientation peak value of TiN thin film comparable to that of (111) orientation (I_{200}/I_{111} for short) was about 0.2; when N_2/Ar ratio increased to 3:7, I_{200}/I_{111} changed to 0.76; I_{200}/I_{111}=3.37 as N_2/Ar ratio was 5:5; when we deposited TiN thin film in pure N_2 atmosphere, we could obtain all-right (200) preferred orientation, I_{200}/I_{111}=13.16.

We can see that, at room temperature, the (200) peak value of TiN thin film was rather stronger than that of the (111) peak (Fig.3). At 200 °C, the (111) and (200) peak values were both enhanced because stress of the thin film was released. When temperature reached 500 °C, the (200) peak value became stronger while the (111) peak value almost disappeared.

It was seen that TiN (200) peak value was enhanced remarkably as the electrical current values increased.

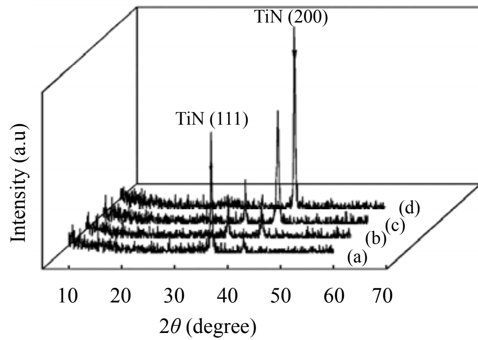

Fig.2 Si (100) substrate, air pressure: 1.5 Pa, substrate temperature: 500 °C, electrical current: 0.8 A
(a) N_2:Ar=1:9; (b) N_2:Ar=3:7; (c) N_2:Ar=5:5; (d) Pure N_2

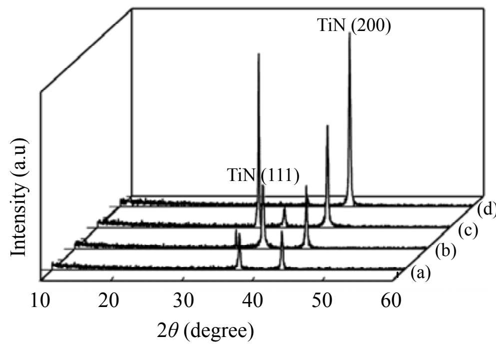

Fig.3 Pure N_2 atmosphere, at different temperature, DC-sputtering TiN thin films
(a) 20 °C; (b) 200 °C; (c) 300 °C; (d) 500 °C

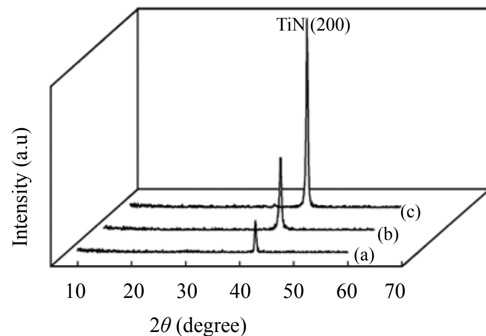

Fig.4 Si (100) substrates, pure N_2 atmosphere, 1.5 Pa air pressure, 500 °C, and DC-sputtering TiN thin films
(a) I=0.8 A; (b) I=1.2 A; (c) I=1.6 A

AFM figures

The surface morphology of the thin films was characterized using an atomic force microscope (Seiko, SPI3800A, AFM) (Fig.5). In each figure of specimen, the two small figures in the left are scanning figures, and the other two in the right are their simulant stereographs. The scanning scales are 2400 nm×2400 nm and 500 nm×500 nm, respectively. We can see that uniformity and roughness were improved as the temperature rose. When the temperature was 500 °C (Fig.5d), the film was compact and uniform.

Electric resistivity measurement

The electric resistivity of specimens was measured by a four-point probe. Square-resistivity was calculated by the following formula:

$$R_S=(R_F+R_R)/2,$$

here, R_S, R_F and R_R are shortened forms of square-resistivity, forward-resistivity and reverse-resistivity, respectively.

Table 1 Resistivity of TiN thin films

Specimens*	a	b	c	d
R_F	6.7	28.9	7.2	15.9
R_R	6.7	28.9	7.1	15.9
R_S	6.7	28.9	7.15	15.9

* Parameters: pure N_2 atmosphere, at different temperature, DC-sputtering. (a) 20 °C; (b) 200 °C; (c) 300 °C; (d) 500 °C

DISCUSSION

TiN_x is stable over a composition range of $0.6<x<1.2$ (Murray, 1987). The (111) plane consists only of titanium atoms or nitrogen atoms. The (200) and (220) planes contain both nitrogen and titanium atoms. The crystalline planar density of TiN is shown in Fig.6. The calculation results of the atomic planar density for each plane are also shown in this figure.

The (200) planes or the square surfaces of the cubic unit cell have the lowest surface energy. This can be explained by a simple bond-breaking model, the (200) planes have the minimum number (per unit area) of out-of-plane Ti-N bonds—the strongest bonds in this structure. The competitive planes are the (200) plane with the lowest surface energy and the (111) plane with the lowest strain energy during the growth of TiN film. The favored equilibrium orientation of sputtered TiN films should be the (200) plane based solely on surface energy considerations. With rising temperature, the surface energy was reduced layer by layer, so that the (200) plane was the

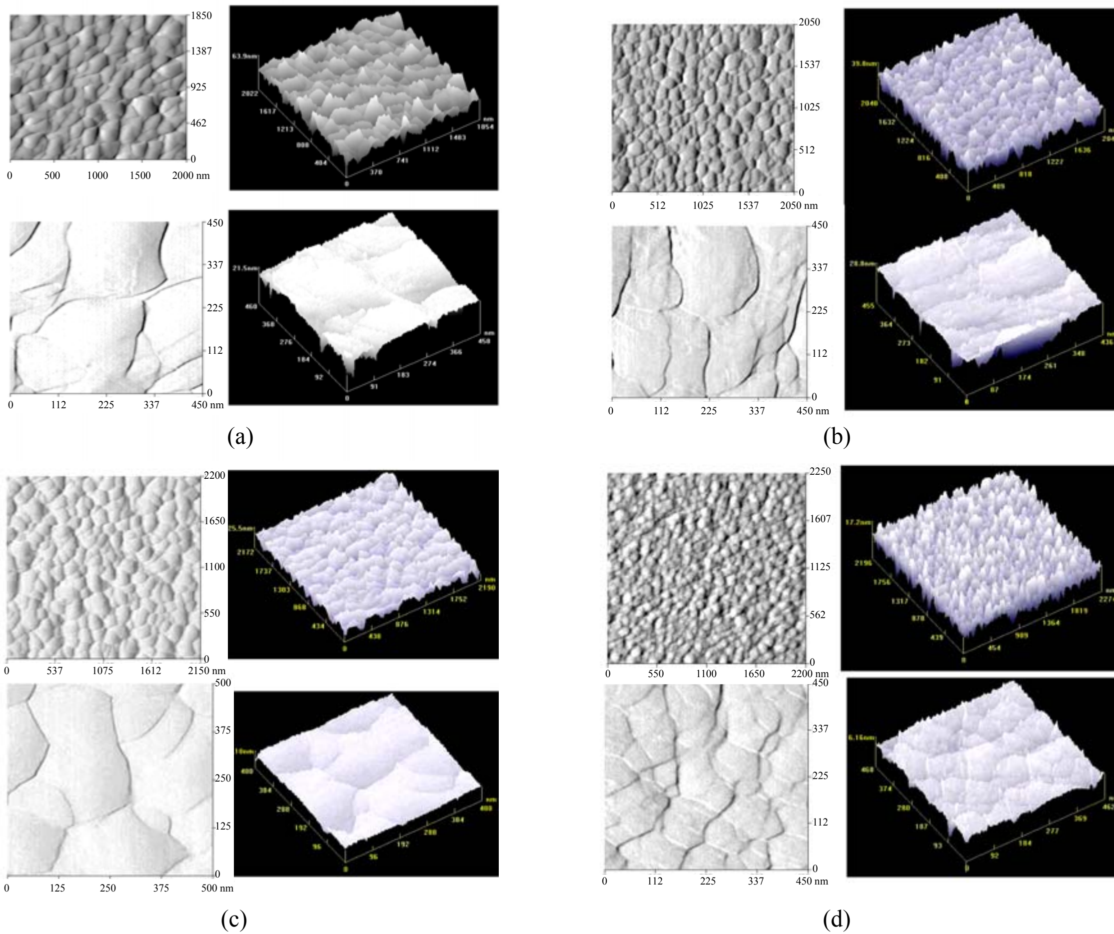

Fig.5 AFM figures of specimens: pure N_2 atmosphere, at different temperature, DC-sputtering TiN thin films. (a) 20 °C; (b) 200 °C; (c) 300 °C; (d) 500 °C

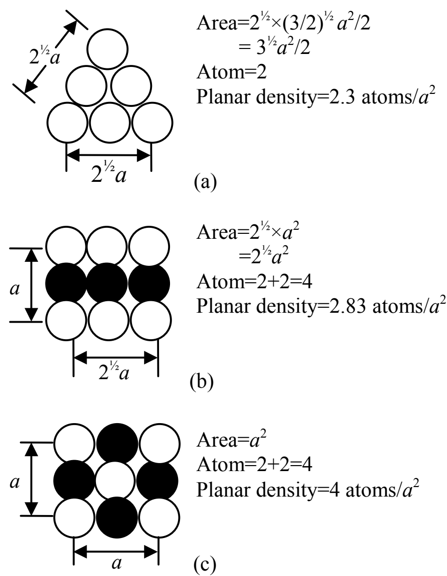

Fig.6 Schematic surface density of different crystalline planes for TiN. (a) (111) plane; (b) (220) plane; (c) (200) plane

primary orientation.

With increasing N_2-content in the sputtering gas mixtures, the sputtering velocity dropped. This would cause the number of atoms arriving at the substrate in unit time to decrease. Therefore the atoms absorbed on the substrate surface had enough time to diffuse and react. Then they released self-reaction energy and reached the lowest surface energy. They would grow along the (200) crystalline plane paralleled substrate. The atoms' later grow would follow that of previous atoms along the (200) crystalline plane. The competitive growth between the (200) crystalline plane and the (111) crystalline plane was stopped (Banerjee *et al*., 2002). When the sputtering gas was pure N_2, in the aura discharge plasma, the percentages of the ionization particles are 96.3% N_2^+, 3.5% N^+, and 0.2% Ti^+, respectively (Hultman *et al*., 1995). For nitrogen molecule ion (N_2^+) which had fixed energy

(20 eV), when the electrical current value of DC sputtering increased, the amount of Ti atoms would increase, and the ion-atom flow ratio of N_2^+/Ti would increase too. The preferred orientation angle of TiN thin films would increase with N_2^+/Ti, the TiN (200) peak value was enhanced remarkably as the electrical current value increased.

CONCLUSION

The results indicate that pure N_2 atmosphere, higher temperature, and higher electrical current values were the key parameters for depositing highly preferred (200) orientation TiN thin films. The surface of TiN thin films was uniform. Their electric resistivity was relatively small, so they are suitable for use as bottom electrodes and diffusion barriers.

References

Arnell, R.D., Colligon, J.S., Minnebaev, K.F., Yurasova, V.E., 1996. The effect of nitrogen content on the structure and mechanical properties of TiN films produced by magnetron sputtering. *Vacuum*, **47**(5):425-431. [doi:10.1016/0042-207X(95)00241-3]

Banerjee, R., Chandra, R., Ayyub, P., 2002. Influence of the sputtering gas on the preferred orientation of nanocrystalline titanium nitride thin films. *Thin Solid Films*, **405**(1-2):64-72. [doi:10.1016/S0040-6090(01)01705-9]

Chen, Y.M., Yu, G.P., Huang, J.H., 2001. Role of process parameters in the texture evolution of TiN films deposited by hollow cathode discharge ion platingtechnol. *Surf. Coat. Technol.*, **141**(2-3):156-163. [doi:10.1016/S0257-8972(01)01201-4]

Chou, W.J., Yu, G.P., Huang, J.H., 2001. Deposition of TiN thin film on Si (100) by HCD ion plating. *Surf. Coat. Technol.*, **140**(3):206-214. [doi:10.1016/S0257-8972(01)01120-3]

Cuniot-Ponsard, M., Desvignes, J.M., Ea-Kim, B., 2003. Radio frequency magnetron sputtering deposition of hetero-epitaxial strontium barium niobate thin films ($Sr_xBa_{1-x}Nb_2O_6$). *J. Appl. Phys.*, **93**(3):1718-1724. [doi:10.1063/1.1535749]

Groudeva-Zotova, S., Kaltofen, R., Sebald, T., 2000. DC reactive magnetron sputter deposition of (111) textured TiN films: influence of nitrogen flow and discharge power on the texture formation. *Surf. Coat. Technol.*, **127**(2-3):144-154. [doi:10.1016/S0257-8972(00)00569-7]

Huang, J.H., Tsai, Y.P., Yu, G.P., 1999. Effect of processing parameters on the microstructure and mechanical properties of TiN film on stainless steel by HCD ion plating. *Thin Solid Films*, **355-356**(1):440-445. [doi:10.1016/S0040-6090(99)00670-7]

Huang, J.H., Lin, C. H., Ma, C.H., Chen, H., 2000. Low energy ion beam assisted deposition of TiN thin films on silicon. *Scripta. Mater.*, **42**(6):573-579. [doi:10.1016/S1359-6462(99)00393-0]

Hultman, L., Sundgren, J.E., Greene, J.E., Bergstrom, D.B., Petrov, I., 1995. High-flux low-energy (20 eV) N_2^+ ion irradiation during TiN deposition by UHV reactive magnetron sputtering: Effects on microstructure and preferred orientation. *J. Appl. Phys.*, **78**(9):5395-5403. [doi:10.1063/1.359720]

Kelly, P.J., Armell, R.D., 2000. Magnetron sputtering: A review of recent developments and applications. *Vacuum*, **56**(3):159-172. [doi:10.1016/S0042-207X(99)00189-X]

Koch, A., Raven, C., Spanne, P., Snigirev, A., 1998. X-ray imaging with submicrometer resolution employing transparent luminescent screens. *Journal of the Optical Society of America A*, **15**(7):1940-1951.

Li, T.Q., Noda, S., Tsuji, Y., Ohsawa, T., Komiyama, H., 2002. Initial growth and texture formation during reactive magnetron. Sputtering of TiN on Si (111). *J. Vac. Sci. Technol.*, **20**(3):583-588. [doi:10.1116/1.1458944]

Murray, J.L., 1987. Phase Diagrams of Binary Titanium Alloys. ASM International, Ohio, p.176.

Sundgren, J.E., 1985. Structure and properties of TiN coatings. *Thin Solid Films*, **128**(1-2):21-44. [doi:10.1016/0040-6090(85)90333-5]