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ARTICLE

Study on Microstructure and Properties of Zr-Si-N Films with Different Nitrogen Partial Pressures

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Abstract: Zr-Si-N films were prepared by radio frequency powered reactive magnetron sputtering at different N_2 partial pressures. The influences of N_2 partial pressure on the microstructure and properties of Zr-Si-N films were studied. The results reveal that the Zr/Si ratio decreases and the sheet resistance increases as the N_2 partial pressure increases. The microstructures of Zr-Si-N films are composed of nano-crystallite ZrN embedded into amorphous matrix of SiN_x phase and a small quantity of Zr_2Si produced at low N_2 partial pressure. The appearance of Zr_2Si phase is related to the low nitridation level. The microhardness of Zr-Si-N film decreases with the increase of N_2 partial pressure at the N_2 partial pressure of 0.03 Pa, the microhardness of Zr-Si-N films is possessed of maximum value of about 22.5 GPa. The phenomenon that high N_2 partial pressure results in low microhardness in Zr-Si-N films may be related to the lattice distortion induced by the addition of Si.

Key words: Zr-Si-N films; magnetron sputtering; microstructure; properties

Transition metal nitrides find wide applications in many sectors, such as diffusion barriers in microelectronics, hard wear resistant coatings on cutting tools, or as corrosion and abrasion resistant layers on optical and mechanical components [1]. Recently, it is frequently reported that some additives such as Al and Si can improve the properties of nitride coatings [2]. In microelectronic field, ternary thin films, such as Ti-Si-N [3] and Ta-Si-N [4] films also exhibit excellent diffusion barriers performance. Veprek and Reiprich [5] suggested that composite materials consisting of crystalline refractory transition metal nitrides such as ZrN, NbN, VN, W_2N and TiN with amorphous Si_3N_4 are the most promising candidate. Although several investigations on the barrier performances and thermal stabilities of Zr-N[6] and Zr-Si-N [7] films were conducted, little research is focused on the microstructure and properties of Zr-Si-N films with different deposition conditions. The present work reveals Zr-Si-N films deposited onto Si wafers and mainly reports the effects of nitrogen partial pressure on the microstructure and properties of Zr-Si-N films.

1 Experimental

Zr-Si-N films were prepared in ultrahigh vacuum reactive magnetron sputtering equipment. The mirror-polished Si (100) wafers were used as substrates and cleaned ultrasonically before they were put into vacuum chamber. The base pressure of vacuum chamber was lower than 10^{-5} Pa and the substrates were firstly cleaned by bombardment of Ar ion. The composite targets consisted of zirconium plate (purity with 99.9%, Φ75 mm×5 mm) and two Si chips (purity with 99.999%, 10 mm×10 mm×0.6 mm) that were stuck on the zirconium plate. The target was sputtered in a mixture of argon and nitrogen (purity with 99.999%) to deposit the Zr-Si-N films. During deposition, the sputtering pressure was 0.3 Pa and the nitrogen partial pressure was 0.03, 0.06 and 0.09 Pa respectively. The bias voltage applied on the substrates was –100 V. The RF power was 200 W and the distance between the target and the substrate was fixed at 80 mm.

The film composition was determined by an Energy Dis-

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persive Spectroscopy (Oxford INCA X-sight). The X-ray diffraction (Regaku D/max-3A) patterns were obtained with CuK α radiation. The microstructure was examined with a Transmission Electron Microscope (JEM-200). The chemical bonding state of Zr-Si-N films was characterized by X-ray Photoelectron Spectroscopy (PHI-5702) using Al-Kα radiation. The sheet resistance and microhardness of Zr-Si-N films was investigated with four-point probe meter (SDY-4) and microhardness tester (MH-5), respectively.

2 Results and Discussion

The EDS analysis reveals that the nitrogen partial pressure has a great effect on the ratio of Zr/Si in Zr-Si-N films. Fig.1 shows the definite relationship between N_2 partial pressure and Zr/Si ratio determined by EDS. The Zr/Si ratio decreases with the increase of N_2 partial pressure from 0.03 to 0.09 Pa. This is related to the different sputtering rates of Si and its nitrides. The Si in a dominant form of low nitridation level would be re-sputtered away by the impinging particles more easily than that in the nitrided form[8]. As the N_2 partial pressure increases the nitridation level of Si also increases, which could decrease the resputtering rate of silicon and result in high Si content.

Fig.2 shows the XRD patterns of Zr-Si-N films. As N_2 partial pressure increases, the intensity of ZrN (111) phase becomes weak gradually but the intensity of ZrN (220) increases. At low N_2 partial pressure of 0.03 Pa, Zr_2Si (202) phase appears. The appearance of Zr_2Si phase is related to the low nitridation level. With the increase of N_2 partial pressure, Zr_2Si phase disappears. There are only diffraction peaks of crystalline ZrN but no signals from crystalline Si_3N_4 or from zirconium silicide can be observed at N_2 partial pressure of 0.06 and 0.09 Pa. This result shows that Si might be present in an amorphous phase of silicon nitride at higher N_2 partial pressure.

The TEM examination of Zr-Si-N films indicates that the grain size in the films is very fine with 20 nm or less and changes little with the variation of N_2 partial pressure.

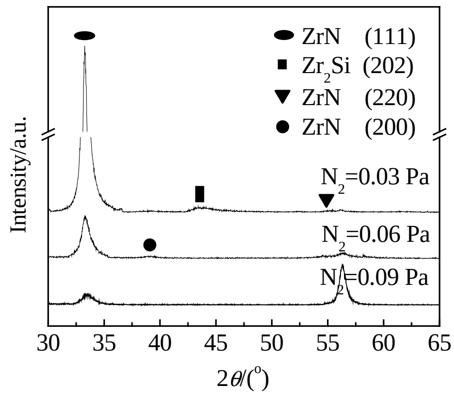

Fig.2 XRD patterns of Zr-Si-N films sputtered with different N_2 partial pressures

Fig.3 is the the TEM bright field (BF) image and electron diffraction (ED) patterns of Zr-Si-N films deposited with the N_2 partial pressure of 0.09 Pa. The diffraction rings can not be seen clearly from the ED patterns. This may be attributed to the very fine grains and amorphous SiN_x existing in the Zr-Si-N film.

The XPS analysis of the chemical state elements can characterize the phase composition in Zr-Si-N films. Fig.4a shows the Zr 3d spectra in Zr-Si-N films. The peak binding energies of Zr-N are consistent with the standard records of stoichiometric ZrN [9,10]. Fig.4b shows the Si 2p spectra in Zr-Si-N films, with the labeled values of standard binding energy of Si_3N_4 and Si. It is noticed that there are no XPS peaks of Zr-Si bonding in the spectra. This may be the result of that the zirconium silicide existing in the Zr-Si-N films is very little. From Fig.4, it can be realized that the majority of Si exists in amorphous SiN_x phase in the Zr-Si-N films.

As a summary, the analyses of XRD, TEM and XPS indicate that the microstructures of Zr-Si-N films sputtered with different N_2 partial pressures are composed of nano-crystallite ZrN embedded into amorphous matrix of

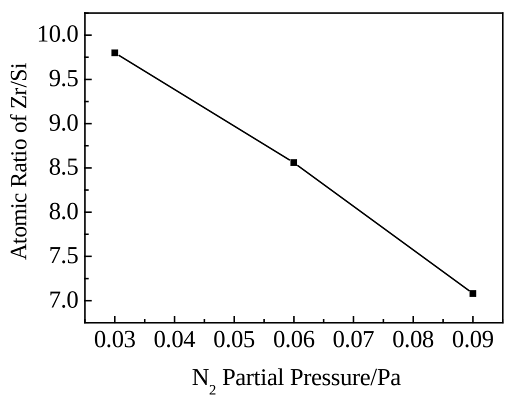

Fig.1 The Zr/Si ratio in Zr-Si-N films sputtered with different N_2 partial pressures

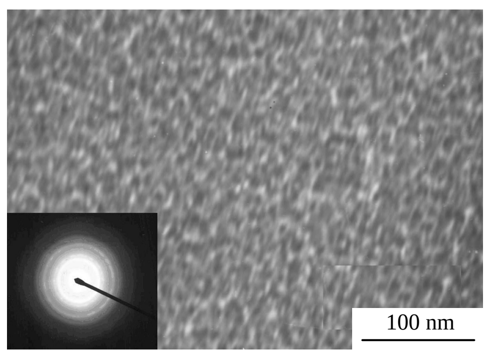

Fig.3 TEM images of Zr-Si-N films sputtered with the N_2 partial pressure of 0.09 Pa

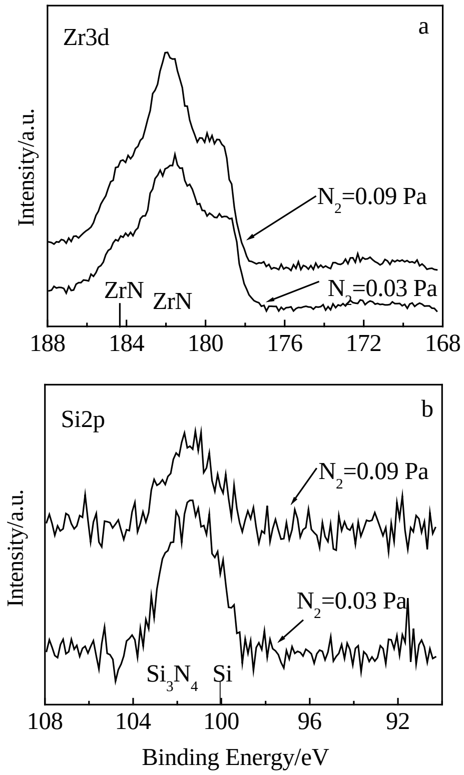

Fig.4 XPS spectra of Zr3d (a) and Si 2p (b) for Zr-Si-N films

SiN_x phase and a small quantity of Zr_2Si produced at low N_2 partial pressure. The appearance of Zr_2Si phase is related to the low nitridation level.

Fig.5 shows the relationship between the N_2 partial pressures and the sheet resistances of Zr-Si-N films. It can be seen that the sheet resistance of Zr-Si-N films increases gradually as the N_2 partial pressure increases. This is related with Si content of the film. The high Si content results in high resistivity of the film. The result is consistent with the similar research of Ta-Si-N films [11].

Fig.6 illustrates that the microhardness of Zr-Si-N films decreases with the increase of N_2 partial pressure. The microhardness reaches the maximum value of about 22.5 GPa at the N_2 partial pressure of 0.03 Pa. Nose M. et al[12] investigated the relationship between the hardness of Zr-Si-N films and Si content. They reported that the hardness of Zr-Si-N films has a maximum value appearing at about 5% Si, and then decreases gradually with the increase of Si content. This variation of hardness in Nose's experiment corresponds well to the change of residual stress and is interpreted in terms of lattice distortion by the addition of Si. In our experiment, the Si content in all of the Zr-Si-N films is more than 5%, and increases with the increase of N_2 partial pressure (Fig.1). Therefore, according to the Nose's interpretation, the phenomenon that the microhardness of Zr-Si-N films decreases with the increase

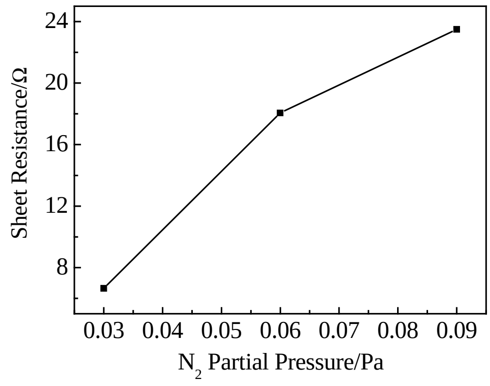

Fig.5 The sheet resistance of Zr-Si-N films sputtered with different N_2 partial pressure

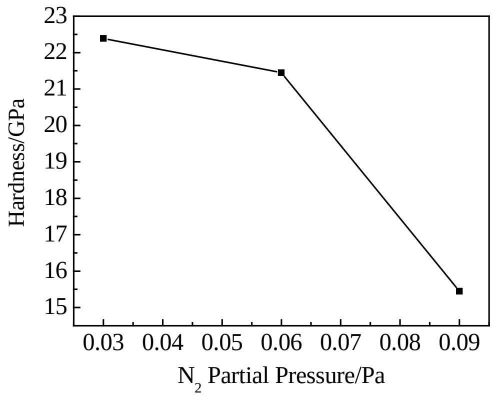

Fig.6 The microhardness of Zr-Si-N films sputtered with different N_2 partial pressure

of N_2 partial pressure in the present experiment may be related to the lattice distortion induced by the addition of Si.

3 Conclusions

The microstructures of Zr-Si-N films are composed of nano-crystallite ZrN embedded into amorphous matrix of SiN_x phase and a small amount of Zr_2Si produced at low N_2 partial pressure. The appearance of Zr_2Si phase is related to the low nitrogen activity. The grain size in the Zr-Si-N films is about 20 nm or less and changes little with the variation of N_2 partial pressure. With the increase of N_2 partial pressure, the Zr/Si ratio decreases and the sheet resistance increases. At the N_2 partial pressure of 0.03 Pa, the microhardness of Zr-Si-N film reaches the maximum value of about 22.5 GPa.

References

1 Hultman L. *Vacuum*[J], 2000, 57(1): 1

2 Feng C, Zhu S, Li M *et al*. *Surface and Coatings Technology*[J], 2008, 202: 3257

3 Ee Y C, Chen Z, Law S B *et a*l. *Applied Surface Science*[J], 2006, 253: 530
4 Hubner R, Hecker M, Mattern N *et al*. *Thin Solid Films*[J], 2006, 500: 259
5 Veprek S, Reiprich S. *Thin Solid Films*[J], 1995, 268(1~2): 64
6 Wang Y, Zhao C, Cao F *et al*. *Materials Letters*[J], 2008, 62: 2289
7 Daniel R, Musil J, Zeman P *et al*. *Surface and Coatings Technology*[J], 2006, 201: 3368
8 Diserens M, Patscheider J, Lévy F. *Surface and Coatings Technology*[J], 1998, 109(1~3): 241
9 Netterfield R P, Martin P J, Mckenzie D R. *Journal of Materials Science Letters*[J], 1990, 9(8): 972
10 Milosev I, Strehblow H H, Navinsek B. *Thin Solid Films*[J], 1997, 303(1~2): 246
11 Olowolafe J O, Rau I, Unruh K M *et al*. *Thin Solid Films*[J], 2000, 365(1): 19
12 Nose M, Zhou M, Nagae T *et al*. *Surface and Coatings Technology*[J], 2000, 132(2~3): 163

不同氮分压制备纳米复合 Zr-Si-N 薄膜的组织与性能研究

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摘　要：利用射频反应磁控溅射设备在不同 N_2 分压下制备了 Zr-Si-N 纳米复合薄膜。研究了 N_2 分压对薄膜组织和性能的影响。结果表明：随着 N_2 分压的增加，薄膜中 Zr、Si 元素含量比降低，且薄膜方电阻增加；Zr–Si–N 薄膜的微观组织由纳米晶 ZrN 嵌入 SiN_x 非晶基体构成，在低 N_2 分压条件下，有少量 Zr_2Si 形成。Zr_2Si 的形成与低 N 反应活性相关。在 0.03 Pa N_2 分压条件下，Zr-Si-N 薄膜硬度达到 22.5 GPa 的最大值。高 N_2 分压制备薄膜硬度较低可能与 Si 原子造成的晶格畸变相关。

关键词：Zr-Si-N 薄膜；磁控溅射；微观组织；性能

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