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Structure and Properties of Ti-Cu-N Films Prepared by ICP Assisted Magnetron Sputtering

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An inductively coupled plasma (ICP) was sustained by an internal coil covered with insulation to assist magnetron sputtering. By this means, the growing films were bombarded by a high-density (~2.0 mA/cm^2) low-energy (~22 eV) ion flux. Then Ti-Cu-N films containing approximately 0-10 at.% Cu were deposited on the grounded Si(100) substrates at a low temperature of 300°C. Film hardness was significantly enhanced by the addition of about 2 at.% Cu and attained a maximum value of approximately 42 GPa. The superhard Ti-Cu-N film was characterized as having a nanocomposite structure, consisting of nanocolumns of TiN crystallites with a dispersion of Cu crystallites around the columnar boundaries. The residually compressive stresses of this series of Ti-Cu-N films were measured to be lower than 1.5 GPa. Thus, the hardness enhancement by the addition of a small amount of Cu was attributable to a nanocomposite effect.

Key words: Sputtering, Inductively coupled plasma, Nanocomposite film, superhardness

1. INTRODUCTION

Hard films have been successfully used to improve the mechanical and tribological properties of tools or machine parts since the 1970s. Much of the early work was focused on the deposition of monolithic transition-metal nitrides or carbides films with hardness of 20-30 GPa [1]. Later studies showed that even superhard (>40 GPa) films, which may satisfy the requirements prompted by the need to develop high speed dry machining for modern industry, can be synthesized when two hard films were deposited alternately to form nanometer scaled multilayer [2]. However, the strong dependence of the hardness on the bilayer thickness may cause large variation in film hardness when coating objects with a complicated shape. This problem can be avoided if the multilayer is replaced by single-layer nanocomposite film [3]. Therefore, in the last few years, the preparation of superhard nanocomposite films has attracted increasing interests. At first, it was believed that superhardness can be achieved only in case when both component phases of the nanocomposite are hard materials [4,5]. Very soon after, it was, however, found that the nanocomposite films, consisting of a hard transition metal nitride with a few at.% of soft metal, i.e., nc-MeN/M` nanocomposites, may also form superhard materials [6-9]. For example, Musil has demonstrated that superhardness can be achieved in nc-ZrN/Cu [6,7], nc-ZrN/Ni [8] and nc-ZrN/Y [9] nanocomposite films. However, during the deposition of the above nc-MeN/M` films, alloy targets were usually used [6-9]. The variation of the content of soft metal phase in these films was then achieved by resputtering with varying degree of ion bombardment. But the bombardment of the growing films with energetic ions is generally apt to induce a large biaxial compressive stress. Hence, the hardness enhancement cannot be solely contributed to the formation of such nanocomposite structures because the measured high values of film hardness might be falsified by the high compressive stress [10,11].

In order to clarify the possibility of achieving superhardness in the nc-MeN/M` nanocomposite film unambiguously due to a nanocomposite structure, two pure elemental targets were employed to avoid the development of a large compressive stress in this study. By bombarding the growing films with a high-density low-energies ion flux through using an inductively coupled plasma (ICP) assisted magnetron sputtering method, superhard nc-TiN/nc-Cu nanocomposite films with small compressive stress (<1.5 GPa) were deposited on the grounded Si(100) substrates. We investigated microstructure as well as the hardness of the Ti-Cu-N films and examined the relationship between the enhanced hardness and the microstructure.

2. EXPERIMENTAL DETAILS

The magnetron sputtering apparatus, which was equipped with two elemental targets, a Ti target and a Cu target (both of 99.99%), was described elsewhere [12]. A one-turn internal coil with insulation coverage was placed in the vicinity of the substrate to sustain an ICP at 300 W. A grid cover was placed in front of the Cu target to limit the amount of Cu atoms impinging onto the substrate, as Cu has much a higher sputtering yield than Ti [13]. The chamber was evacuated to about 5×10^{-4} Pa and then a gas mixture of argon and nitrogen (both of 99.998% purity) was injected. Gas flow rates of argon and nitrogen were 10 and 2 sccm, respectively. Total deposition pressure was maintained at 0.5 Pa. By fixing the sputtering current of the Ti target at 0.8 A and varying that of the Cu target from 0 to 0.14 A, a series of Ti-Cu-N films containing 0-10 at.% Cu with a thickness of about 500 nm were prepared on the grounded Si(100) substrates at a low deposition temperature of 300°C.

An energy-resolved quadrupole mass spectrometer (Hiden EQP system) was used to analyze the energy distribution of the incident ion flux at the substrate. The chemical composition of the films was determined by electron probe microanalysis (EPMA) with ZAF correction method (JXA-8600, JEOL, Japan). The crystal microstructures were identified by X-ray diffraction (XRD) with a θ-2θ goniometer (Miniflex, Rigaku, Japan) and transmission electron microscopy (TEM, TOPCN EM-002B). Film morphology of the cross section was obtained by field-emission scanning electron microscopy (FE-SEM S-4500, HITACHI Co., Japan). Film stress was estimated from the bending of the Si substrate. Film hardness was measured by a nanoindentation system (Triboscope, Hysitron Inc.) with an impression depth lower than 10% of film thickness. Before the indentation, fused quartz, which has a hardness value of 10 GPa, was used as a standard sample to carefully calibrate the tip shape function.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical energy spectra of the incident $^{40}Ar^{+}$, $^{28}N_2^{+}$ and $^{48}Ti^{+}$ ions at the grounded substrate. It reveals that the mean energy of the ion flux is approximately 22 eV. The high-energy tails of the spectra never extend beyond 30 eV.

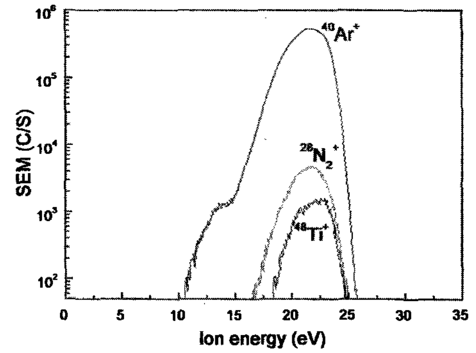

Fig.1 Typical energy spectra of the incident ions (300W).

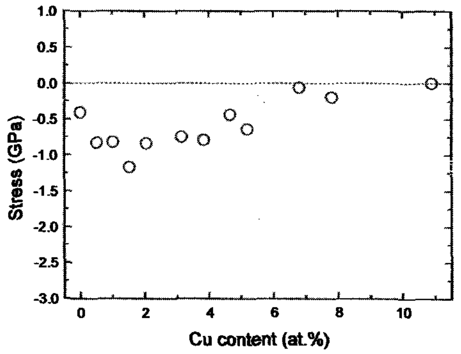

Fig.2 Residual stress as a function of Cu content.

At such a low ion energy, the atomic penning effect, which is believed to be the main reason for the development of a large compressive stress in thin film, can be suppressed significantly, and then resulting in a low residual stress [14-16]. Figure 2 shows the residual stress of these Ti-Cu-N films as a function of Cu content. From this figure, it can be seen that the maximum compressive stress is smaller than 1.5 GPa.

Nanoindentation results reveal that the incorporation of Cu atoms into TiN films significantly modifies the mechanical properties. Figure 3 shows the dependence of film hardness on Cu content. The hardness of the pure TiN is approximately 22.8 GPa. By adding a small amount of Cu content, film hardness increases significantly, and attains a maximum value of 42 GPa at approximately 2 at.% Cu. This value is nearly two times higher than that of pure TiN. With further increasing the Cu content, film hardness rapidly drops to a value even lower than that of the pure TiN.

It has been reported that the hardness of the PVD-grown TiN film typically increases by 2-3 GPa when compressive stress increases 1 GPa [17]. Thus, the significant enhancement of the hardness in this study cannot be attributable to the compressive stress. It should be attributed to a microstructure effect.

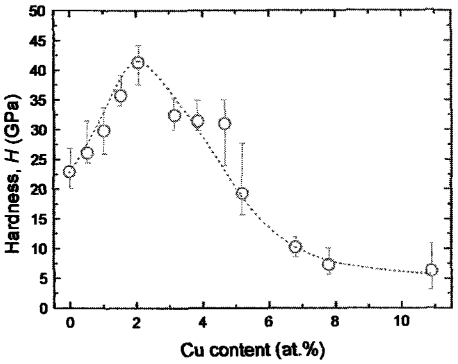

Fig.3 Hardness as a function of Cu content.

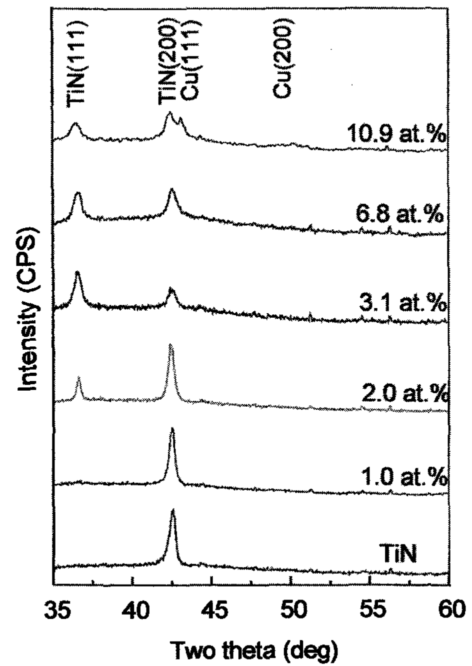

Fig.4 X-ray diffractograms of the Ti-Cu-N films.

Figure 4 shows the XRD patterns of the Ti-Cu-N films containing various Cu contents. It can be seen that there are strong tendencies of decreasing the peak intensity, deteriorating the TiN(200) preferred orientation and appearing additional diffraction line upon an increase in the copper content in these films.

As shown in Fig.4, the pure TiN film exhibits a preferred orientation in the crystalline plane of (200). This is different from the most PVD-grown TiN films, which generally reveal a preferred orientation of (111) due to a competitive growth [18]. Since TiN(200) plane is the lowest surface energy face of TiN [19], the (200) surface is expected to be the preferred orientation at elevated growth temperature where the surface mobility of adatoms are sufficient to form crystallites bounded by low-energy planes during nucleation and/or liquidlike coalescence [20]. In other words, the appearance of the (200)-preferred orientation in the pure TiN film in Fig.4 implies that the deposition condition used in this study more closely approaches the thermodynamic equilibrium synthesis condition [20]. Thus, it is reasonable to assume that under this condition the added Cu atoms can kinetically segregate to form a separate phase. Actually, the diffraction peaks that can be assigned to crystalline Cu appear in the XRD patterns of the films with higher content of Cu. Fig.4 also reveals that the addition of a small amount of Cu will weaken the (200)-preferred orientation. The film containing 3.1 at.% Cu exhibits a random orientation.

With respect to the films containing lower content of Cu, the Cu-associated diffraction peaks are not observed in their XRD patterns. In general, the absence of Cu reflection implies that either the Cu may not segregate to form a separate phase or the separate phase may be amorphous or the size of Cu crystallites and/or their quantity is too small to be detected by XRD method due to the limits of detection resolution [6]. However, based on the following reasons: (1) TiN and Cu are immiscible materials under thermodynamic equilibrium conditions and the deposition condition can assure that the segregation of Cu occurs kinetically; and (2) no TiN (200) peak shift in XRD with the addition of Cu is evident in Fig.4; and (3) only a small amount of Cu leads to a loss of the (200)-preferred orientation; it is believed that the Cu do segregate instead of dissolving into the B1 lattices in the films containing lower Cu.

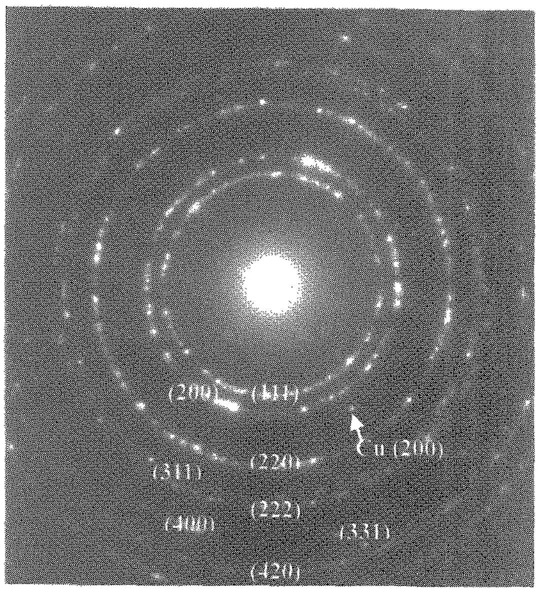

Fig.5 Electron diffraction patterns of the Ti-Cu-N films containing 2.0 at.% Cu.

Musil has suggested that in the Zr-Cu-N system, the segregated Cu might exist as a thin layer of amorphous matrix surrounding the ZrN grains [6]. If a similar structure can be formed in the Ti-Cu-N system, the wettability of TiN by Cu should be very good. However, It has been reported that the Cu did not wet the stoichiometric TiN [19]. Since the atomic ratio of Ti to N is nearly 1.0 in the series of Ti-Cu-N films (not shown here), it is unlikely that the Cu exists as a thin layer of amorphous matrix in these Ti-Cu-N films. Thus, it is rational to assume that the Cu exists as very tiny crystallites rather than amorphous matrix in the Ti-Cu-N films with lower content of Cu.

To confirm this assumption, selected-area electron diffraction (SAD) patterns were performed. Figures 5 show the cross-sectional SAD patterns from the hardest Ti-Cu-N film that contains about 2.0 at.% Cu. In agreement with its XRD pattern, the diffraction rings verify the existence of crystalline TiN. Additionally, the electron diffraction pattern corresponding to the crystalline Cu can also be observed. It means that the Cu is codeposited as crystalline Cu phase.

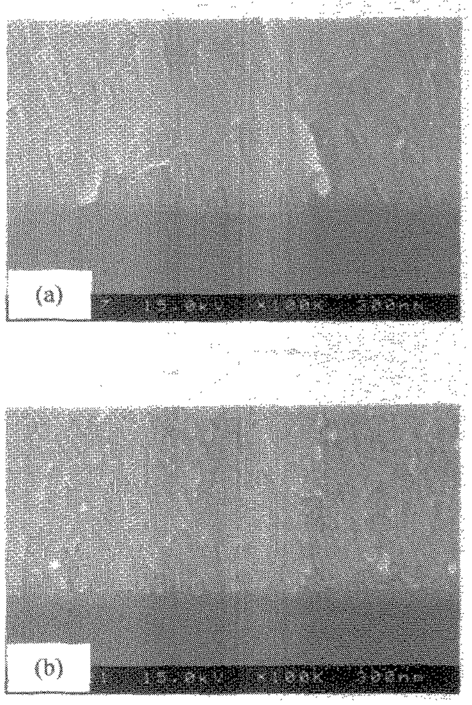

Fig.6 FESEM images of the Ti-Cu-N films containing (a) 2.0 at.% Cu, and (b) 3.1 at.% Cu.

The morphology of the Ti-Cu-N films depends strongly on the Cu content, as shown in Fig.6. These FE-SEM images were observed on the fracture surface (cross section) of these films. The hardest film that contains about 2.0 at.% Cu exhibits a columnar structure. With the addition of up to 3.1 at.% Cu, the columnar structure abruptly transforms to a globular-like structure. The texture evolution can be explained by using the structure zone model (SZM) by Barna and Adamik for dual-phase films [22-24]. According to this SZM, the segregated Cu crystallites dispersing around the TiN grains inhibit the growth of TiN crystallites, and hence resulting in a loss of the (200)-texture.

From the above results, it can be assumed that the hardest film that contains 2.0 at.% Cu has a pronounced TiN(200) texture, in which very tiny Cu crystallites are distributed around the columnar boundaries of TiN crystallites. Thus, the hardening mechanism by the formation of a solid solution [25] or by the formation of nc-TiN/a-Cu nanostructure [6] can be obviated to explain the hardness enhancement in our study. Myung has suggested that the hardness enhancement of Ti-Cu-N films by the addition of a small amount of Cu could be attributable to the finer size of TiN crystallites due to the growth impediment by the Cu phase [26]. However, the crystallite sizes of the films containing less than 2 at.% Cu nearly remain at ~22 nm and the average size of TiN crystallites for the hardest film is still ~19 nm, as shown in Fig.7. Therefore, the hardening by finer size in term of the Hall-Petch relationship is not applicable to the present series of Ti-Cu-N films either.

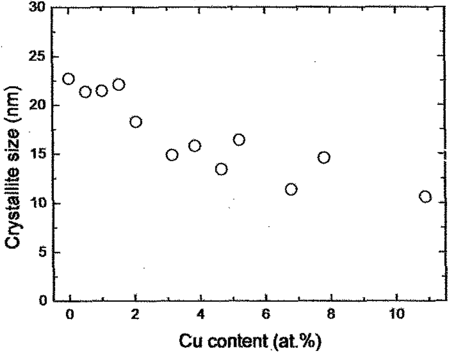

Fig. 7 Crystallite size of the Ti-Cu-N films as a function of the Cu content.

In fact, the investigations on single-phase TiN imply that the hardness of TiN does not depend strongly on the grain size [1]. The existence of a weak grain boundary was generally suggested as the reason [1]. The weak columnar grain boundaries in TiN films usually become the sites for crack initiation and propagation under stress [27,28]. It has been reported that during wearing the films with a columnar structure, the pre-existing cracks along the columnar grain boundaries would increase in number and length in the initial wear process [28]. Therefore, it is reasonable to assume that these pre-existing cracks along the columnar grain boundaries are attributable to the premature failure of TiN film. Thus, the hardening mechanism by the addition of a small amount of Cu is probably due to shortening of the flaw size present along the columnar boundaries of TiN crystallites after deposition by the dispersion of very tiny Cu particle. By shortening the crack length along the columnar boundaries, fracture strength and hardness increase as suggest by the Griffith criterion [29].

Here, it is noteworthy that the hardness enhancement due to the dispersion of nc-Cu [30], or nc-Ni [31], or nc-W [32] in Al_2O_3 matrix has also been reported in bulk ceramic nanocomposites. Thus, the statement that the hardness improvement is due to the dispersion of nanocrystallites of soft metal instead of the formation of amorphous metal matrix [6] may be of general validity.

4. CONCLUSION

Superhard Ti-Cu-N films were deposited at a low temperature by the ICP assisted magnetron sputtering. The hardness reached to a maximum value of 42 GPa at approximately 2 at.% Cu. The hardest Ti-Cu-N films was characterized as having a nc-TiN/nc-Cu structure with a pronounced TiN(200) texture, in which very tiny Cu nanocrystallites dispersed around the nanocolumns of TiN crystallites. The hardness enhancement was attributed to the formation of the nc-TiN/nc-Cu (not nc-TiN/a-Cu) nanocomposite structure.

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