



Solid solution coating of (TiVCrZrHf)N with unusual structural evolution

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ABSTRACT

In this study, we investigated the microstructure of (TiVCrZrHf)N multi-element coating deposited on Si(100) substrate by magnetron sputtering system. Interestingly, the film showed an unusual structure evolution. A continuous and amorphous initial (TiVCrZrHf)N layer formed on the substrate. As film thickness increased, randomly oriented small (TiVCrZrHf)N grains formed, followed by the development of columnar grains with FCC crystal phase. In contrast to previous studies, the nitride coatings grew on substrates with a 270-nm amorphous interlayer. Under appropriate parameters, the occurrence of the unusual microstructure could be attributed to the sluggish diffusion of the multi-principal components. The maximum hardness of 33.5 GPa was obtained when coating was deposited under substrate bias of -100 V and at substrate temperatures of 723 K.

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1. Introduction

The synthesis of novel multi-principal component nitride coatings, such as (AlCrTaTiZr)N [1], (AlCrNbSiTiV)N [2], and (AlMoNbSiTaTiVZr)N [3], has attracted extensive research interest due to their excellent physical and chemical properties, which are expected to be superior to those of binary or ternary nitride coatings. From a thermodynamics perspective, the high mixing entropies contributed by multi-principal components are believed to stabilize the existence of simple solid solution structures. A single FCC solid solution structure has been reported for multi-principal component nitrides. From a kinetics perspective, large lattice distortions caused by differently-sized atoms lower the diffusion rates of atoms and thus reduce the growth rate of crystallites [4–6]. The resulting coatings are of great interest as potential hard coatings because of their good mechanical properties due to lattice distortions and solid solution strengthening. In addition, they have also received considerable interest as diffusion barriers for Cu interconnections. Further research and development can yield coatings with various functions and great potential for application in different fields [7].

Recently, (TiVCrZrHf)N coatings with five strong nitride forming elements were designed to deposit strong nitride coatings by reactive radio-frequency (RF) magnetron reactive sputtering [8–11]. Material selection was based on the properties of individual binary nitride. Ti and Cr were selected as constituents, since TiN and CrN have been widely used as protective surface coatings due to their satisfactory mechanical properties. To further improve thermal stability, oxidation resistance,

and corrosion resistance, Zr and Hf were incorporated into cubic nitride structure because of their great negative free energy of formation. The addition of V into TiN and CrN had demonstrated low friction coefficient due to the solid state lubricious properties of vanadium oxides. In previous studies, the (TiVCrZrHf)N coatings exhibited a simple FCC structure and that their five metallic elements were in a near-equimolar ratio (not shown). According to the rule of mixtures, the lattice spacing (0.253 nm) of the (TiVCrZrHf)N approximated the average of the fcc (111) planes of TiN, VN, CrN, ZrN, and HfN. This finding exhibited the formation of a simple solid solution with an fcc structure from constituent nitrides and confirmed the effect of high entropies on the simplification of crystal structures. Depth profiling analyses of elemental distributions (SIMS, ION-TOF TOF.SIMS IV) confirmed the homogeneity of the coating composition through layer thickness (not shown). The (TiVCrZrHf)N coating demonstrated superior mechanical properties and high thermal stability. The extremely high hardness value of 48 GPa [8] confirmed that it has great potential for hard and protective coatings. The excellent thermal stability at 800 °C without silicide formation showed that the (TiVCrZrHf)N coating is a promising diffusion barrier material for Cu interconnection [11]. However, the special structural evolution of the (TiVCrZrHf)N coating has not been investigated yet in detail. According to previous reports, the special structural evolution become more significant when (TiVCrZrHf)N coating was deposited at high substrate temperature and high substrate bias voltage. Thus, this manuscript is dedicated to the microstructural evolution of a film deposited at high temperature and high bias voltage as a function of its thickness.

2. Experimental

The (TiVCrZrHf)N coatings were deposited on p-Si(100) wafers by a reactive radio-frequency magnetron sputtering system using

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equimolar TiVCrZrHf targets that were 75 mm in diameter. Prior to deposition, Si substrates were cleaned and rinsed with ethanol and distilled water in an ultrasonic bath. The sputtering chamber was pumped down to 2.67×10^{-4} Pa using a turbo pump. (TiVCrZrHf)N coatings were deposited at a plasma power of 350 W in an Ar + N₂ mixed atmosphere under a working pressure of 6.67×10^{-1} Pa. Flow rates of Ar and N₂ were maintained at 100 and 4 sccm, respectively. The distance between the substrate and target was 90 mm. Morphology was examined using field emission scanning electron microscopy (SEM, JEOL JSM-6700F). Microstructure and local composition were investigated by field emission transmission electron microscopy (TEM, FEI E.O. TecnaiF20) equipped with energy-dispersive spectroscopy (EDS) at an acceleration voltage of 200 kV. The chemical composition was determined by field-emission electron probe micro-analyses (FE-EPMA, JEOL JXA-8800M). The residual stress was determined by using the laser technology via measuring the substrate curvature and applying Stoney's equation for calculation. The nanohardness of the coatings was measured using a TriboLab nanoindenter (Hysitron).

3. Results and discussion

Fig. 1 shows the SEM micrographs of the as-grown (TiVCrZrHf)N coating deposited with different substrate temperatures and biases. Their deposition time was set at 60 min. Coatings without substrate bias revealed a typical V-shaped columnar structure with a faceted surface feature. When a bias was applied, the coating appears less defined but has a more densified columnar structure. These phenomena have been observed and explained in detail by our previous reports [8,9]. Interestingly, a very thick and featureless interlayer near the substrate was found when substrate bias and heat were applied. The thickness of the amorphous layer increased with the addition of the substrate bias voltage and substrate temperature. In order to analyze structure formation and its evolution, subsequent TEM characterizations were performed for a more detailed evaluation of microstructures. The nanohardness of the (TiVCrZrHf)N deposited at various processing parameters is listed in Table 1. The coating without a substrate bias and heating have a relative low hardness. As substrate bias and temperature increased, the hardness also increased. This is reasonable, because the coatings were more densified with the application of substrate biases and temperature [8,9]. The maximum hardness of 33.5 GPa was achieved when coating was deposited under substrate bias of -100 V and at substrate temperatures of 723 K. This demonstrates a moderate substrate bias and temperature to be necessary to obtain a good hard coating.

Cross-sectional TEM micrographs of as-grown (TiVCrZrHf)N coating deposited under substrate bias of -100 V and at substrate

Table 1

The stress and hardness of the (TiVCrZrHf)N deposited at various processing parameters.

Process parameter	Stress (GPa)	Hardness (GPa)
0 V, 723 K	0.62	10.0 ± 3.0
-50 V, 723 K	-2.14	22.5 ± 2.7
-100 V, 723 K	-5.11	33.5 ± 0.6
-150 V, 723 K	-5.32	32.6 ± 0.6
-200 V, 723 K	-5.94	32.4 ± 1.1
-100 V, RT	-5.62	24.5 ± 1.6
-100 V, 623 K	-5.35	32.9 ± 0.8
-100 V, 823 K	-5.01	32.5 ± 0.4

temperatures of 723 K are shown in Fig. 2. To fulfill the requirements of hard coating application, the (TiVCrZrHf)N coating was deposited at approximately $1.4 \mu\text{m}$. There was a continuous change in structure of the (TiVCrZrHf)N coating through its whole thickness. Image contrast revealed that the coating had two distinct layers separated by a boundary (Fig. 2a). The four selected area diffraction (SAD) patterns were labeled as Zones A, B, C, and D. Zone A shows a mixed pattern of spots formed in Si wafer and halo ring. Zone B also has a halo ring. These findings confirm that the structure near the substrate is amorphous. Noticeably, there are two extra spots around the (000) diffraction spot in Zone B, indicating a periodic arrangement. Zone C contains arc-like FCC rings and a (200)-axis structure perpendicular to the substrate misaligned at $\sim 50^\circ$. With increased coating thickness, this preferred orientation perpendicular to the substrate was transformed from (200) to (220). This angle of misalignment initially decreased and then became constant as coating thickness was further increased. Zone D contains a larger single grain SAD with (220)-axis FCC structure (Fig. 2c–f). These results are consistent with the observation of TEM dark-field image (Fig. 2b).

The HRTEM images of as-grown (TiVCrZrHf)N coating deposited under substrate bias of -100 V and at substrate temperatures of 723 K are presented in Fig. 3. An amorphous native oxide layer existed on the surface of the Si substrate. The (TiVCrZrHf)N layer grows on the substrate with a thick amorphous interfacial layer (Fig. 3a and b). Coincident with the SAD analysis in Fig. 2d, there is a layering amorphous structure with layer thickness of 2.29 nm between the amorphous and columnar regions (Fig. 3b inset). EDS analysis did not reveal any visible composition segregation, which may be due to the limited resolution. A more detailed investigation of the layering amorphous structure is still necessary. Fig. 3c and d shows HRTEM images near the bottom and upper part of the V-shaped column, respectively. Nanometer [200] out-of-plane oriented columns can be observed above the

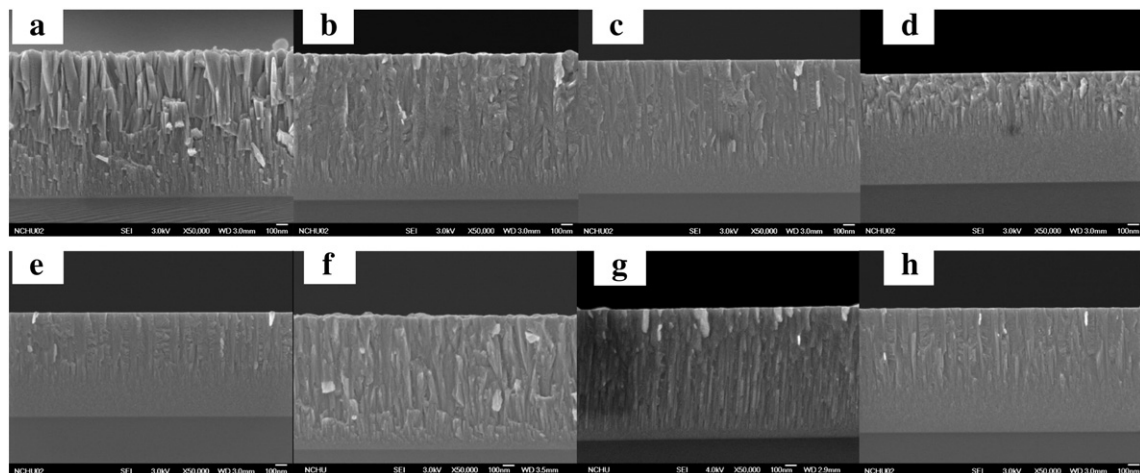


Fig. 1. The SEM micrographs of the as-grown (TiVCrZrHf)N coating deposited under different bias and at different substrate temperatures (a) 0 V, 723 K; (b) -50 V, 723 K; (c) -100 V, 723 K; (d) -150 V, 723 K; (e) -200 V, 450 °C; (f) -100 V, RT; (g) -100 V, 623 K; (h) -100 V, 823 K.

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