Negative effect of vacancies on cubic symmetry, hardness and conductivity in hafnium nitride films

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ABSTRACT

Although vacancies exist commonly in nonstoichiometric transition metal nitrides, their roles on structure and properties are not yet well explored. We show that in rocksalt hafnium nitride films creation of nitrogen and hafnium vacancies leads to an asymmetrical lattice contraction and distortion from cubic to rhombohedral structure owing to the presence of strong texture and compressive stress, and also causes decrease in hardness because of reduction in bulk modulus and decrease in electrical conductivity due to reduction in electron relaxation time. This new insight into vacancy-induced "negative effect" is demonstrated through good matches between our experiments and theoretical calculations.

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Group-*IVB*, *VB* and *VIB* transition metal nitride films crystallizing in rocksalt structure (δ-TMN$_x$, TM = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) have attracted much attention [1–3] recently in both tribological and electronic fields because of their high hardness [4–6], electrical conductivity [2,7], corrosion resistance [8,9], good thermal stability [10–12] and diffusion barrier properties [13–15]. These make them very promising candidates for applications in electronic devices, cutting- and machining-tool industries. In these applications, the mechanical and electrical properties of the films are of utmost importance, as these properties determine the service life and ultimate performances of the devices. It is therefore crucial to understand how to control them.

In δ-TMN$_x$ films, the point defects related to stoichiometry x usually present because of experimental difficulties in obtaining the nominally stoichiometric films ($x = 1$) [16–18]. Nitrogen and metal vacancies are found to commonly exist in the sub-stoichiometric ($x < 1$) and over-stoichiometric ($x > 1$) films, respectively, and have significant influence on the structure, mechanical and electrical properties of the films [19–22]. Although extensive researches on the role of the vacancies have been carried out and numerous results have been reported

[23–32], the following three questions still remain unanswered: (I) Do the vacancies indeed induce lattice contraction? If so, does it occur uniformly along all crystallographic directions? Theoretical studies showed that N vacancies could cause shrinkage of rocksalt lattice [23–25]. However, the impact of metal vacancies is still unclear. The details on the vacancy-induced lattice contraction still lacks direct experimental observations. (II) What is the fundamental role that the vacancies play on the hardness? The effect of vacancies on hardness is still controversial. Some experiments revealed nitrogen vacancies caused increase in hardness [26,27], while others claimed the opposite [28,29]. (III) How do the nitrogen and metal vacancies influence electrical conductivity of the film? Is there difference between effect of the nitrogen vacancies and that of the metal vacancies? Studies show that nitrogen vacancies and metal vacancies are capable of increasing and decreasing electron concentration [30–32], respectively, meaning that they thus should cause increasing and decreasing electrical conductivity, respectively. But is this the case in reality?

With the above three questions in mind, we prepared rocksalt hafnium nitride (δ-HfN$_x$) films containing nitrogen vacancies (V_N) and hafnium vacancies (V_{Hf}), respectively, and carried out three aspects of studies by employing the first-principle calculations in combination of the measurements of structure, hardness and conductivity: (I) confirmation of the existence and the details of the vacancy-induced lattice contraction; (II) identification of the

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contribution of vacancies to hardness; and (III) clarification of the effect of V_N and V_{Hf} on electrical conductivity and their differences. Our experiments and calculations agree well with each other, proving three points: (I) both V_N and V_{Hf} indeed cause lattice contraction, but the contraction is not uniform; (II) incorporation of either V_N or V_{Hf} into HfN lattice accompanies decrease in film hardness; and (III) both V_N and V_{Hf} decrease electrical conductivity (different from their influence on the concentration of free electrons). The mechanisms behind the evolutions in structure, mechanical and electrical properties are discussed in detail.

The HfN$_x$ films were prepared by radio-frequency sputtering a pure Hf target in mixed discharge of argon and nitrogen, and their composition and phase structure were controlled by nitrogen flow rate. The single-phase δ-HfN$_x$ films were obtained by changing nitrogen flow rate from 2.4 to 6.0 sccm when the argon flow rate, power, work pressure, substrate bias and substrate temperature were kept at 80 sccm, 150 W, 1.0 Pa, -80 V and 200 °C, respectively, which induced variation of x from 0.809 to 1.165. V_N and V_{Hf} were primary point defects in sub-stoichiometric δ-HfN$_x$ films ($0.809 \leqslant x \leqslant 0.989$) and over-stoichiometric films ($1.039 \leqslant x \leqslant 1.165$), respectively, which were identified by employing the first-principle calculations in combination with the experiments of Raman, high-resolution transmission electron microscopy (HRTEM), concentration of free electrons and interband transition absorption spectra, which were reported in detail in Ref. [32]. HRTEM was used for observation of lattice images, X-ray diffraction (XRD) and selected area electron diffraction (SAED) for identification of crystal structure and measurement of lattice parameters, nano indentation and probe measurements for characterization of hardness and conductivity. The residual stresses in the films were calculated using Stoney equation [33], $\sigma_f = \frac{E_s t_s^2}{6(1-\nu_s)r t_f}$, where elastic modulus (E_s), thickness (t_s) and Poisson's ratio (ν_s) of silicon substrate are 190 GPa, 0.5 mm and 0.272, respectively. The curvature (r) and thickness (t_f) of the films were determined using a Dektak150 surface profiler. For each sample, the hardness, elastic modulus, stress and conductivity tests were performed for six, six, two and three times, respectively. The reported results represent the average values. Density functional theory calculations were performed to investigate the structure and mechanical properties of the defective and non-defective δ-HfN$_x$. The details of preparation, characterization and computation methods were reported elsewhere [32].

Fig. 1 plots XRD spectra and SAED patterns for δ-HfN$_x$ films containing V_N ($0.809 \leqslant x \leqslant 0.989$) and V_{Hf} ($1.039 \leqslant x \leqslant 1.165$), respectively. From the GIXRD spectra (Fig. 1a) and SAED patterns (Fig. 1d–f), four diffraction peaks and rings attributed to (111), (200), (220) and (311) in rocksalt phase appear simultaneously, indicating that the films remain in the rocksalt structure when x varies from 0.809 to 1.165. From the symmetric $\theta/2\theta$ XRD spectra (Fig. 1b), all samples contain one strong δ-HfN (111) peak and one weak δ-HfN (200) peak. The intensity ratio between these two peaks is approximately 5:1, far higher than 1.5:1 of the intensity ratio calculated from the ICDD PDF card (No. 65-0923), indicating that the films were strongly textured in $[111]$ direction. Compare to the 2-theta values of ICDD PDF card (No. 65-0923), all of 2-theta values of (111), (200), (311) and (220) peaks in our XRD spectra shift to lower angles, indicating the high levels of residual stress. Peak position is also influenced by vacancy formation. As x increases, the vacancy concentration in the films initially decrease and then increase, which results in 2-theta values first decreasing and then increasing, thus leads to the overall position change of XRD peaks appeared insignificant in Fig. 1a and b. Consistent evidence from GIXRD, SAED and XRD results converges to point to one thing: incorporation of V_N or V_{Hf} into HfN lattice does not change its rocksalt structure. Neither does it change the (111) texture of the films.

Fig. 1c shows the lattice parameter (a) obtained from GIXRD patterns for δ-HfN$_x$ films with different x. In order to compare to the experiments, the theoretical lattice parameter obtained by first-principles calculations for δ-HfN$_x$ containing V_N and V_{Hf} are also given in Fig. 1c. For sub-stoichiometric HfN$_x$ films, a decreases slowly as x decreases from 0.989 to 0.809. This trend agrees well with theoretical results, thus confirms that the introduction of V_N causes a lattice contraction. For over-stoichiometric films, a shows a sharp reduction with increasing x from 1.039 to 1.165, indicating that the V_{Hf} results in a large lattice contraction. The experimental and theoretical results (Fig. 1c) consistently show that a of over-stoichiometric HfN$_x$ films decrease more significantly with x variation compared to sub-stoichiometric HfN$_x$ films, indicating the lattice contraction arisen from V_{Hf} is more pronounced than that from V_N. Fig. 2a–c display the HRTEM lattice images for the near-stoichiometric HfN$_{1.039}$, sub-stoichiometric HfN$_{0.809}$ and over-stoichiometric HfN$_{1.165}$ films, respectively. In the near-stoichiometric film, the interplanar distances (d) of (111) and (200) planes are found to be $d_{111} = 0.269$ nm and $d_{200} = 0.231$ nm (Fig. 2a). However, they were reduced to $d_{111} = 0.266$ nm and $d_{200} = 0.230$ nm with the formation of V_N (Fig. 2b). When V_{Hf} are created in the HfN lattice, these interplanar distances sharply decreased to $d_{111} = 0.264$ nm and $d_{200} = 0.228$ nm (Fig. 2c). These observations are in good agreement with XRD results, proving that both V_N and V_{Hf} lead to lattice contraction and the contraction induced by V_{Hf} is more remarkable than that by V_N due to almost 3 times of atomic size difference: the atomic radius of Hf is 2.16 Å while that of the N is only 0.75 Å.

It is noted from Fig. 1c that (111) planes have much larger lattice parameters (a_{111}) than other planes such as (200), (220) and (311) for a given x. This means that the spacing of (111) planes is relatively expanded as compared to other planes, and the lattice undergoes deformation along $[111]$ direction. In order to better identify the type and extent of lattice distortion, we have measured the angles between the typical crystallographic planes via fast Fourier transform (FFT) based on the HRTEM image. The corresponding results are shown in Fig. 2d–f. For a perfect stoichiometric HfN crystal, the two angles between (111) and (200) planes and between (111) and $(1$-1-$1)$ planes are 54.7° and 109.5°, respectively. Interestingly enough, in all of our HfN$_x$ films the first angle gets larger, while the second one becomes smaller. In the near-stoichiometric HfN$_{1.039}$ (Fig. 2d) the first and second angles are 55.3° and 108.2° with an increase of 1.1% and decrease of 1.2% respectively as compared to them in the perfect HfN crystal. In the case of V_N-containing HfN$_{0.809}$ (Fig. 2e), the two angles are sharply increased and reduced to 56.5° (an increase of 3.3%) and 107.1° (a decrease of 2.2%), respectively. For V_{Hf}-containing HfN$_{1.165}$ film (Fig. 2f), the two angles are further increased and reduced to 58.3° (an increase of 6.6%) and 106.5° (a decrease of 2.7%), respectively, and the extent of lattice distortion is further enhanced. The HRTEM and XRD results prove that the spacing of (111) planes of our HfN$_x$ films are relatively expanded compared to the other planes and certain lattice distortion takes place.

To identify the type of lattice distortion observed experimentally when the spacing of (111) planes is dilated, we have carried out the first-principle calculations. To simulate the (111) plane expansion, we have theoretically applied an outward force perpendicular to the (111) planes, making the spacing of (111) planes increased gradually. The results are shown in Fig. S1 in the Supporting Material. As the (111) spacing expands, the other planes undergo distinct contraction, causing a lattice distortion from cubic to rhombohedral structure. For a better analogue to our experiments, we measured the two angles between (111) and (200) planes and between (111) and $(1$-1-$1)$ planes, and find that as (111) planes gradually expand, that is, a_{111} increases, the