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ScienceDirect

Acta Materialia 90 (2015) 59–68

Acta MATERIALIA

www.elsevier.com/locate/actamat

Identification and thermodynamic mechanism of the phase transition in hafnium nitride films

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Received 27 January 2015; accepted 13 February 2015

Abstract—A stoichiometry-driven phase transition from rocksalt to “nitrogen-rich” structure exists in *group-IVB* transition metal nitride films. As this phase transition is critical in controlling the film properties it has attracted numerous studies. However, researchers are still divided with regard to the structural identity of this “nitrogen-rich” phase, not to mention detailed exploration of the phase transition mechanisms. In this study, we confirmed that the “nitrogen-rich” phase in hafnium nitride (HfN_x) films had a cubic Th_3P_4 structure of space group symmetry of $I\text{-}43d$ (220), namely $c\text{-}Hf_3N_4$. The confirmation was obtained by combining the first-principle calculations with a series of experiments: Selected Area Electron Diffraction, High Resolution Transmission Electron Microscopy, Raman, Gracing Incident X-ray Diffraction and X-ray Photoelectron Spectroscopy. The mechanisms of the phase transition were elucidated through calculations on enthalpy of formation (*EOF*). The experimental results agree well with the theoretical calculations. We conclude that with increasing nitrogen, phase transition takes place from rocksalt (δ-HfN) to $c\text{-}Hf_3N_4$ through three stages of structural evolution: δ-HfN (containing Hf vacancies) → mixture of (δ-HfN + $c\text{-}Hf_3N_4$) → $c\text{-}Hf_3N_4$. The driving force of the phase transition is energy minimization. The three stages of structural evolution are explained by comparing the *EOF* of the δ-HfN and $c\text{-}Hf_3N_4$ phases. As the phase transition takes place, the hafnium nitride film morphs from a conductive and opaque metal into an insulating and transparent semiconductor.

Keywords: Transition metal nitrides; Phase transition; Structure; Mechanism; Stoichiometry

1. Introduction

Transition metal nitrides are well known as a class of fascinating and technologically important materials in the fields of electronic devices, cutting- and machining-tool industry [1–3]. Among them, hafnium nitride (HfN_x) and zirconium nitride (ZrN_x) films have attracted much attention recently [4–6] because of their high electrical conductivity, large “phononic band gap”, small real permittivity, high infrared reflectance coupled with high abrasion, corrosion resistance and thermal stability [7–10]. These make them very promising candidates for use as counter electrode in dyesensitized solar cells [11], hot carrier solar cell absorber [12], alternative plasmonic materials [13], solar control coatings on windows [14], decorative coatings [15], as well as reflecting back contacts in solar cells [5,16] and light-emitting-diode (LED) devices [17]. In these applications, electric and optical properties are of utmost importance. ZrN_x and HfN_x films exist in various phase structures thus present different electric and optical properties [14,18]. To obtain tailored properties for desired applications, therefore, it is crucial to understand how to control the phase structure.

Stoichiometry (x) is an important factor in determining phase structure [14,18,19]. Extensive studies confirm that near-stoichiometric ($x = 1.00$) HfN_x and ZrN_x films are of a thermodynamically most stable rocksalt structure [20]. In this structure, the films are optically opaque, gold-like in color, highly infrared reflecting as well as electrically conductive [14,17]. Interestingly, as x increases from ~1.00 to ~1.33, a phase transition from rocksalt structure to a so-called “nitrogen-rich” phase takes place [21]. Different from rocksalt phase, the films with “nitrogen-rich” phase are optically transparent and electrically

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http://dx.doi.org/10.1016/j.actamat.2015.02.026
1359-6462/

insulating, plus many novel physical properties [22–24]. Obviously this phase transition is important for controlling the properties of the films thus attracting numerous studies. Still, the following three problems remain concerning the identity of the "nitrogen-rich" phase and the mechanisms of the phase transition: (i) What exactly is this "nitrogen-rich" phase? Some believed it was the orthorhombic structure (o-TM_3N_4) [18,25–27], some thought it was the cubic Th_3P_4 structure (c-TM_3N_4) [24,28–30], others believed that it was still the rocksalt structure [31,32], but this rocksalt structure contained some point defects and lattice distortion (δ-TM_3N_4). (ii) How does the rocksalt phase of $x = 1/1$ transform to the "nitrogen-rich" phase of $x = 4/3$? Does it occur gradually or abruptly? Studies show that stoichiometry of the films can be continuously increased by increasing the nitrogen flow rate, or manipulating other deposition conditions [24,33,34]. In these reports, the phase structures corresponding to a different stoichiometry are not identified, and the details of the transition are unrevealed. (iii) Why does the phase transition take place? i.e., what is the driving force? So far, the mechanisms on phase transition are still not well explored.

With the above three questions in mind, we sputtered HfN_x films with different x through controlling of nitrogen flow rate, and carried out three aspects of studies by employing the first-principle calculations in combination of the structural measurements, namely, Selected Area Electron Diffraction (SAED), High Resolution Transmission Electron Microscopy (HRTEM), Raman, Gracing Incident X-ray Diffraction (GIXRD) and X-ray Photoelectron Spectroscopy (XPS). These studies are: (i) identifying structure of the "nitrogen-rich" phase of the HfN_x films; (ii) elucidating the structural evolution process from rocksalt to "nitrogen-rich" phase; and, (iii) clarifying the phase transition mechanism by calculating the enthalpy of formation (*EOF*) at different x. These three aspects of studies are discussed in detail in Sections 3.1, 3.2 and 3.3, respectively. Our experiments and calculations agree well, thus proving three points: (i) This "nitrogen-rich" phase of HfN_x films has a cubic Th_3P_4 structure (i.e., c-Hf_3N_4); (ii) The phase transition from rocksalt (δ-HfN) to c-Hf_3N_4 is not an abrupt but a gradual transition process of three distinct stages of structural evolution; (iii) The driving force of the phase transition is energy minimization; all these three stages of structural evolution are well explained by comparing the *EOF* of the δ-HfN and the c-Hf_3N_4 phases.

2. Experimental and computational details

2.1. Preparation and characterization of the HfN_x films

HfN_x films with a thickness of about 600 nm were simultaneously deposited on single-crystal Si (001) wafers and optical glass substrates by radio-frequency (RF) reactive sputtering a pure Hf target in the mixed discharge gases of Ar and N_2 [35]. The distance between the target and substrate holder was fixed at 55 mm, and the chamber was evacuated by a turbomolecular pump to 4×10^{-4} Pa prior to deposition. Prior to entry into the vacuum chamber, the Si wafer and the glass substrates were cleaned ultrasonically in acetone, alcohol and distilled water, consecutively. During the deposition, the flow rate of Ar and N_2 was accurately controlled by independent mass flow controllers. Stoichiometry x in HfN_x films was varied from 1.039 to 1.334 by increasing the flow rate ratios of $N_2/(Ar + N_2)$ from 3% to 50% while the RF power, work pressure, substrate negative bias and substrate temperature were kept constant at 150 W, 1.0 Pa, −80 V and 200 °C, respectively. X-ray diffraction (XRD) measurements were carried out in both symmetric $\theta/2\theta$ and grazing-incidence (GIXRD) modes of a Bruker D8tools X-ray diffractometer using Cu Kα as the incident radiation. The microstructure of the films was characterized using a high-resolution transmission electron microscope (HR-TEM, JEOL TEM-2010). The stoichiometry x and core-level spectra of the films was determined by XPS measurements (VG ESCA LAB MKII), in which a monochromatized Al Kα (1486.6 eV) X-ray source was used, and Ar^+ cleaning procedure lasting 180 s was applied to all samples prior to XPS quantitative analysis to remove possible adventitious carbon and absorbed oxygen from the sample surface. Raman measurements (T64000 (Horiba)) were obtained by using a 633 nm line Ar^+ laser excitation with a laser power of 200 mW, and an accumulation time of 30 s under the frequency range of 50–1600 cm^{-1}. The transmission spectrum in the range of 300–2500 nm was obtained by a PerkinElmer Lambda 900 Ultraviolet–visible–near infrared (UV–vis–NIR) spectrometer. The optical gap of the films was determined by plotting $(\alpha h\nu)^2$ against the photon energy $h\nu$ according to the Tauc equation. The film thickness was determined by using a $Dektak^3$ surface profile measuring system.

2.2. Computational methodology

Density functional theory (DFT) calculations were performed to explore the electronic structure of the defective and non-defective HfN_x in the rocksalt structure and Hf_3N_4 in cubic Th_3P_4 structure. The method of projector-augmented wave potentials was employed as implemented in the Vienna ab initio simulation package (VASP) code [36,37]. The generalized gradient approximation (GGA) with the parametrization of Perdew–Burke–Ernzerhof (PBE) was used to express the exchange–correlation energy of interacting electrons [38]. The kinetic energy cutoff of 550 eV was used for the plane wave expansion. The Monkhorst–Pack method was used to sample the k points. The Brillouin zones are sampled with the high-density Γ-centered k-point grid. The spin-polarization effect has been considered in the calculation. The introduction of point defects in HfN_x does not induce the localized magnetic moment nor result in the spin-polarization. The calculated lattice constant of pristine HfN of space group Fm-3m is 4.53 Å, very close to that from the measurements (~4.58 Å). To model high- and low-point defect concentration, one or two Hf vacancies are considered in the ideal 8-, 12-, 16-, 18-, 24-, and 32-atom HfN cells. A 28-atom supercell was used in modeling the cubic-Th_3P_4-structured Hf_3N_4 of space group *I*-43*d*. The calculated lattice constant is 6.69 Å, very close to that from the measured (~6.71 Å).

3. Results and discussion

3.1. Structure identification of the "nitrogen-rich" phase

Fig. 1a and b plots the Selected Area Electron Diffraction (SAED) patterns of the near-stoichiometric