Applied Surface Science 433 (2018) 306–311

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

The growth of the metallic ZrN_x thin films on P-GaN substrate by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 23 June 2017
Received in revised form
21 September 2017
Accepted 30 September 2017
Available online 3 October 2017

Keywords:
Zirconium nitride
Pulsed laser deposition
Metallic
Reflectivity
p-GaN

ABSTRACT

Although metal nitride thin films have attractive prospects in plasmonic applications due to its stable properties in harsh environments containing high temperatures, shock, and contaminants, the effect of deposition parameters on the properties of the metallic ZrN grown on III-N semiconductors by pulse laser deposition still lacks of detailed exploration. Here we have successfully prepared metallic ZrN_x films on p-GaN substrate by pulsed laser deposition in N_2 ambient of various pressures at a fixed substrate temperature (475 °C). It is found that the films exhibit quite smooth surfaces and (111) preferred orientation. The X-ray photoelectron spectroscopy measurements indicate that carbon contamination can be completely removed and oxygen contamination is significantly reduced on the film surfaces after cleaning using Ar^+ sputtering. The N/Zr ratio increases from 0.64 to 0.75 when the N_2 pressure increases from 0.5 Pa to 3 Pa. The optical reflectivity spectra measured by the UV–vis–NIR spectrophotometer show that the ZrN_x is a typical and good metallic-like material and its metallic properties can be tuned with changing the film compositions.

1. Introduction

Since the early 1970s, transition metal nitrides have been considered as a super-hard material for protective coatings [1–3]. Over the years, its electronic properties have been also extensively studied for alternative applications, such as diffusion barriers in microelectronic devices [4–7], ohmic contacts on III-nitride semiconductors [8–11], and Schottky contacts on Si due to its compatibility with CMOS technology [12]. Recently, transition metal nitrides, such as titanium nitride (TiN) and zirconium nitride (ZrN), have been appealing for plasmonic devices due to its superior physical properties compared to the traditional noble metals, like gold and silver [13,14]. They have low carrier concentration, and consequently, the magnitude of their real permittivity is much smaller than that of noble metals in the visible range [15,16]. Additionally, they belong to ceramic materials that are non-stoichiometric and hence their properties combine metal-like and covalent characteristics [16]. Unlike the case for noble metals, their optical properties may be tuned simply by changing the processing conditions [16]. Another major advantage is the high melting point, especially when in nanoparticle form, making them suitable candidates for application in photothermal devices, optical sensors and flat photonic components, e.g. ultrathin lenses operated in harsh environments containing high temperatures, shock, and contaminants [17–19].

At present, there have been a lot of researches on the applications of TiN as plasmonic material [16–21]. However, it is worth noting that ZrN films have shown higher hardness, better corrosion resistance and higher thermochemical stability compared to the TiN films [22]. The durability and refractory properties of ZrN also make it an ideal material for plasmonic applications. Though various approaches have been made for growth of high quality ZrN thin films [23–31], the structure and properties of the ZrN thin film are strongly dependent on the preparation methods. In this study, we have prepared the metallic ZrN_x thin films on c-plane p-GaN substrate by pulsed laser depositon (PLD). We comprehensively investigated the effect of the total N_2 pressure in deposition chamber on the structure, morphology, composition and optical properties of ZrN_x thin films. The crystal structure and morphology of the films are characterized by X-ray diffraction and atom force microscopy. Then, for full understanding the composition and chemical bonding states of the deposited ZrN_x films, the X-ray photoelectron spectroscopy analysis is performed. In addition,

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https://doi.org/10.1016/j.apsusc.2017.09.262
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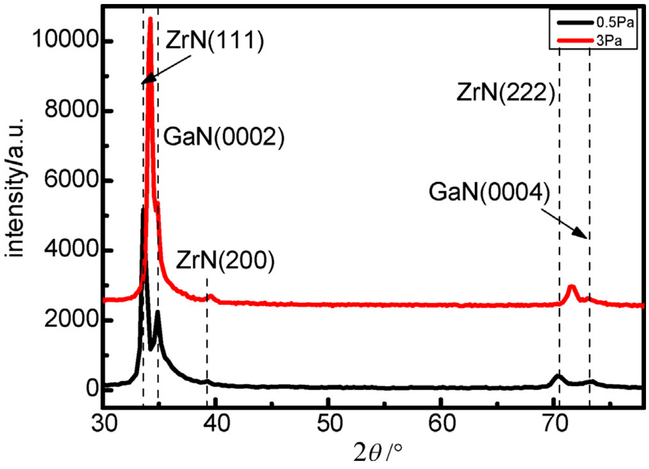

Fig. 1. XRD 2θ-ω spectra for as-grown ZrN_x thin films grown at different nitrogen pressure.

the optical reflectivity spectra of the films are recorded between 200 nn and 1800 nm using UV–vis–NIR spectrophotometer.

2. Experimental section

The experiments were carried out in a high-vacuum system of up to 2.0×10^{-7} Pa using a KrF excimer laser (248 nm wavelength, 25 ns pulse duration, 10 HZ pulse repetition rate). A nominally stoichiometric polycrystalline ZrN target of 99.5% purity was used and placed in parallel to the substrate at a distance of 70 mm. The ZrN thin films were deposited on c-plane Mg-doped GaN substrate, which was grown on c-plane sapphire by metal organic chemical vapor deposition (MOCVD). Before being loaded into the deposition chamber, the substrate was ultrasonically cleaned for 3 min successively in acetone, alcohol, and deionized water, and then blown dry in pure N_2 gas. After transferring the substrates into the deposition chamber, the chamber was evacuated to 5.0×10^{-6} Pa by a turbo molecular pump. A laser beam was focused on the rotated ZrN target at an incidence angle of 45°. In order to remove the contaminated surface layer of the target, it was presputtered for about 10 min. During deposition, the laser beam energy was set at 350 mJ with a pulse repetition of 2 Hz. The substrate temperature was fixed at 475 °C. The deposition of the ZrN thin films was carried out in high-purity nitrogen (99.999%) ambient with pressure at 0.5 Pa and 3 Pa.

3. Results and discussion

The crystal structure and growth orientation of as-grown ZrNx films with a thickness of 40 nm were examined by X-ray diffraction(XRD, Bruker Advance diffractometer with a Cu kα1 X-ray source, $\lambda = 1.5406$ Å). Fig. 1 shows the XRD 2θ-ω scan results for ZrN_x thin films grown at different nitrogen pressure. The ZrN_x films exhibit NaCl-type cubic structure and (111) preferred orientation with very weak (200) reflection. The (0002) peak of the wurtzite GaN are next to the right side of the (111) peak of the ZrN_x. According to Bragg's law, it can be concluded that the in-plane lattice parameter of c-GaN is slightly smaller than that of ZrN_x(111), which means the lattice mismatch between ZrN(111) and c-GaN is small (1.6%) [30]. Particularly, it can be found that the positions of the diffraction peaks of the ZrN_x films shift towards the higher angles with the increase of the nitrogen pressure, inferring that the lattice constant of the ZrN_x films decreases with increasing the nitrogen pressure. The lattice constant (a) for the ZrN_x films grown at different nitrogen pressure is calculated by using the following Eqs. (1) and (2):

$$d_{hkl} = \frac{\lambda}{\sin(\theta_{2h2k2l} + \Delta\theta)} = \frac{\lambda}{2\sin(\theta_{hkl} + \Delta\theta)} \quad (1)$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

where (hkl) are the indices of the diffraction plane, θ_{hkl} is the measured angular position of the (hkl) reflection, $\Delta\theta$ is the zero error of the instrument, and λ is the X-ray wavelength (1.5406 Å for Cu kα1radiation). The lattice mismatch between the ZrN_x(111) and c-GaN is obtained by using Eq. (3) [32]:

$$\delta = \frac{\frac{\sqrt{2}}{2}a - a_0}{a_0} \quad (3)$$

where δ is the lattice mismatch between the ZrN_x(111) and c-GaN and a_0 is the in-plane lattice constant of GaN. The in-plane lattice constant of the strain-free GaN is $a_0 = 3.189$ Å [30]. The calculated lattice constant of the ZrN_x thin films is 4.647 Å and 4.5845 Å, respectively, and the lattice mismatch is corresponding to 3% and 1.6%. This means that the lattice mismatch between the ZrN_x(111) and c-GaN gradually decreases with increasing the nitrogen pressure. Moreover, the average grain size and the lattice strain are calculated using the Williamson–Hall Plot, the employed formula is as followed [33]:

$$\frac{\beta\cos\theta}{\lambda} = \frac{0.9}{D} + \frac{4\sin\theta\varepsilon}{\lambda} \quad (4)$$

where, β is the instrumental corrected full width at half maximum (FWHM), θ is Bragg's angle, λ is the wavelength of Cu kα1 radiation (1.5406 Å), D is the average grain size and ε is the lattice strain.

The average grain sizes and lattice strain of films obtained from the intercept and slope of the straight line of the Williamson–Hall Plot are found to be 32.2 nm and 2.67×10^{-3}, 29.6 nm and 1.74×10^{-3} at 0.5 Pa and 3 Pa, respectively. The results show the average grain size and lattice strain slightly reduce with increasing the nitrogen pressure.

The Atom Force Microscopy (AFM, Veeco Dimension 3100) was employed to evaluate the surface morphology of as-grown ZrN_x films. Fig. 2a–b shows 3D 1×1 μm^2 AFM images for ZrN_x films grown at various nitrogen pressure. These results show that the root-mean-square (RMS) surface roughness is only 0.286 nm and 0.180 nm, respectively, indicating smooth surfaces for the ZrN_x films. Combined with XRD results, it can be demonstrated that the ZrN_x films grown at different nitrogen pressure are of high quality.

To understand the composition and chemical bonding states of the ZrN_x film grown at various nitrogen pressure, the X-ray photoelectron spectroscopy (XPS, PHI 5000 versaprobe II) measurements were performed using a monochromatic Al kα X-ray source (1486.7 eV). The C1s peak position was adjusted to 284.8 eV for energy calibration of all the spectra to compensate the surface charge effect. The deconvolution of the peaks was carried out using CasaXPS program, in which the peak fitting was performed using Gaussian–Lorentzian peak shape and Shirley type background subtraction.The deconvoluted spectra of Zr3d and N1s are displayed in Fig. 3a–b. As shown in Fig. 3a, the Zr3d signal of the ZrN_x film grown at 0.5 Pa contain four peaks corresponding to 179.26 eV, 180.36 eV, 182.04 eV and 184.54 eV in binding energy, respectively; the Zr3d signal of the ZrN_x film grown at 3 Pa also include four peaks located at 179.11 eV, 180.07 eV, 181.78 eV and 184.19 eV, respectively. According to the literature, the Zr3d binding energy of ZrN in XPS lies between 179.8 eV and 180.0 eV [34,35]. Besides, it has been reported that the binding energy of the Zr3d peak in ZrN_x will go from 179.6 eV to 180.6 eV with increasing the nitrogen partial pressure [36]. Obviously, the values centered at 179.26 and 179.11 eV in