

Crystal Growth of MnS buffer layer for non-polar AlN on Si (100) deposited by RF-magnetron sputtering

Kouta Tatejima^{1,2}, Takahiro Nagata², Keiji Ishibashi^{2,3}, Kenichiro Takahashi^{2,3}, Setsu Suzuki³, Atsushi Ogura¹ and Toyohiro Chikyow⁴

¹ Meiji University, 1-1-1 Higashimita, Tama-ku, Kawasaki, Kanagawa 214-8571, Japan

² International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Phone: +81-29-860-4546 E-mail: NAGATA.Takahiro@nims.go.jp

³ COMET.Inc, 5-9-5 Toukoudai, Tsukuba, Ibaraki, 300-2635, Japan

⁴ Materials Data & Integrated System (MaDIS), NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Abstract

We investigated growth conditions of MnS thin film on Si(100) substrates deposited by RF-magnetron sputtering method for epitaxial growth of non-polar AlN thin film. The insertion of 20 nm MnS film deposited at room temperature on a Si(100) 4 °-off substrate improved the crystallinity and surface roughness of (100) oriented MnS layer with the total film thickness of 50 nm, which is suitable for the crystal growth of AlN.

1. Introduction

GaN shows remarkable optical and electric properties, and has a promising potential for new power electronics devices. In the practical applications such as LED, the polar plane GaN crystal with hexagonal symmetry on c-plane sapphire or Si (111) substrates has been used [1,2]. The c-axis GaN LED device shows the green gap issue that is the emission efficiency decrease at 500 – 600 nm wavelength owing to the quantum-confined Stark effect (QCSE) by piezoelectric polarization [3,4]. To overcome this issue, non-polar or semi-polar GaN devices has been proposed. In addition, to realize non-polar GaN and AlN on Si(100) substrate, we have proposed the MnS buffer layer insertion between AlN and Si [3-7]. MnS has a cubic structure that is identical with Si(100), and lattice constant is near to a-axis length of Si, c-axis and $\sqrt{3}$ times a-axis length of AlN. Consequently, the MnS buffer layer can lead to epitaxial growth of non-polar AlN film. Furthermore, this substrate structure can be expected that non-polar GaN vertical devices, because MnS buffer layer can control conductivity. By employing the MnS buffer layer, we have already demonstrated the epitaxial growth of non-polar AlN film on Si(100) deposited by pulsed laser deposition (PLD) method, and confirmed the effect of room-temperature-grown MnS buffer layer (hereafter, RT-MnS) on the crystallization [3-7]. However, from the view point of the cost efficiency and practical manufacturing process on a large diameter substrate, sputtering method is preferable to PLD method. In addition, we found issues of controllability of surface roughness of MnS films deposited by PLD method owing to the 3-dimensional crystal growth. In this work, to realize the epitaxial growth of non-polar AlN film on Si(100) with MnS buffer layer deposited by sputtering method, crystal growth of MnS film was investigated.

2. Experimental procedure

Si(100) and Si(100) 4 °-off substrates were treated by HF solution after cleaning of organic solvent solution. MnS films were deposited by RF-magnetron sputtering on Si substrates under a base pressure of 6.7×10^{-6} Pa. The substrate temperatures were set as 550 and 700 °C, based on the crystallization temperature of MnS and the epitaxial growth temperature of AlN on a sapphire substrate, respectively. For MnS, a sintered ceramics target was used. RF-power was 150 W, and sputtering Ar gas pressure was 2.0 Pa. The total film thickness of MnS was set as 50 nm. The film thicknesses of RT-MnS were ranged from 1.5 to 20 nm. AlN films were deposited by RF-magnetron reactive sputtering method on MnS buffer layer. A 3-nines Al metal plate was used as a target. For AlN, the substrate temperature was 700 °C. RF power was 100 W. sputtering gas pressure was 0.5 Pa, and the sputtering gas ratio of N₂ to Ar based gas mixture was 14%.

The crystal structure and epitaxial relationship were investigated by 2-dimensional X-Ray diffraction method (2D-XRD). Using 2D-XRD, a part of the Debye Sherrer ring is two-dimensionally detected. The 2 θ and χ angles can be simultaneously detected. The full width at half maximum value of χ angle indicates the mosaicity of films. The surface morphology was observed by atomic force microscope (AFM). The chemical bonding states were characterized by X-ray photoelectron spectroscopy (XPS) using a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV) with a total energy resolution of 700 meV. The obtained XPS data were calibrated against the Au 4f_{7/2} peak, and the Fermi level of Au was set at the same ground level as the sample.

3. Result and discussion

At first, the effects of Si(100) 4 °-off substrate on the thin film growth were considered, which can be expected to control anisotropical strain for the growth of non-polar AlN. Figure 1 shows 2D-XRD images of MnS films with the 1.5 nm thick RT-MnS. The MnS film on the Si(100) 4 °-off substrate indicated stronger and narrower spot diffraction peak corresponding to (200) reflection than that on the Si(100) substrate, suggesting that the high oriented thin film was obtained. The crystallization and surface roughness of the MnS film on Si(100) 4 °-off substrate is more preferable to that on Si(100) substrate. From here, all MnS films were deposited on

Si(100) 4 °-off substrate. However, surface roughness, root-mean-square (RMS) value of MnS film deposited on 4 °-off substrate with the 1.5 nm thick RT-MnS was about 6.0 nm, which inhibited the crystal growth of AlN layer. To improve the surface roughness, effects of the film thickness of RT-MnS on surface roughness was investigated. Note that the 50 nm thick RT-MnS films annealed 700 °C showed the RMS value of 2.1 nm although these films had rotated domain structures. This result suggested that the high temperature deposition induced surface roughness. In contrast, RT-MnS can lead to improve surface roughness. The thickness of RT-MnS were set as 10 and 20 nm. Figure 2 shows AFM images of MnS films deposited at 550 and 700 °C with 10 and 20 nm thick-RT-MnS. RMS values of MnS films with 10 nm thick RT-MnS were still high, more than 4.0 nm. In contrast, MnS films with 20 nm thick RT-MnS indicated improvements of surface roughness and large grain growth. Furthermore, all sample showed similar crystallinity with the (100) oriented structure.

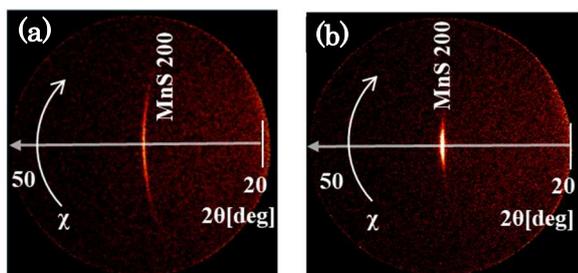


Fig. 1 2D X-ray diffraction images of MnS films deposited on (a)Si(100) and (b)Si(100) 4 °-off substrates.

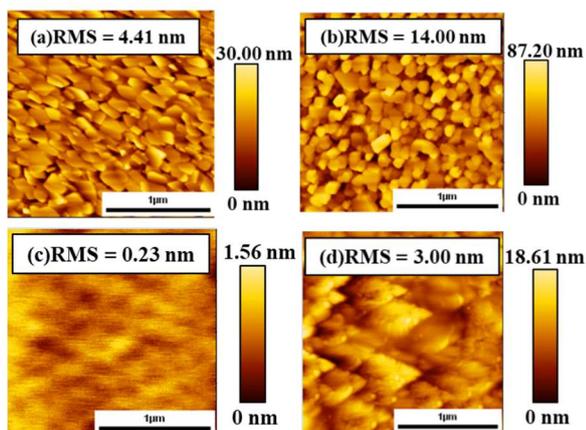


Fig. 2 AFM images of 50 nm thick-MnS films with 10 nm thick-RT-MnS deposited at (a) 550 and (b) 700 °C, and with 20 nm thick-RT-MnS deposited at (c) 550 and (d) 700 °C.

A thermal gap between MnS and AlN growth temperatures may effect on sulfur vacancy formation, which may cause a sulfur contamination into AlN. To confirm the sulfur vacancy formation during the deposition and the ramp-up process of substrate heater, XPS measurement was performed. Figure 3 shows a S 2p spectrum of the MnS film. Four chemical bonding states corresponding to Mn-S and unintentionally oxidized Mn-S_x (Mn-S-O_x) bonds were confirmed. Mn-

S-O_x means that sulfur vacancies oxidized by air exposure. Sulfur vacancies were estimated by the area intensity ratio of three Mn-S-O_x peaks to Mn-S peak (Mn-S-O_x/ Mn-S). The 1.5 nm thick-RT-MnS indicated a high intensity ratio of 0.6 owing to additional oxidization of Si at the interface confirmed by Si 2p spectra corresponding to the SiO₂ bonding state. In contrast, other samples with the thickness over 10 nm and MnS films annealed at 700 °C indicated the ratio of approximately 0.3, meaning that the Mn-S bonds ate stable at the maximum temperature of 700 °C.

The AlN film deposition on the MnS film with 20 nm thick RT-MnS was also performed. The crystallization of AlN was confirmed although AlN films were mainly c-plane oriented films. In the presentation, the growth condition optimization of AlN layer also will be discussed.

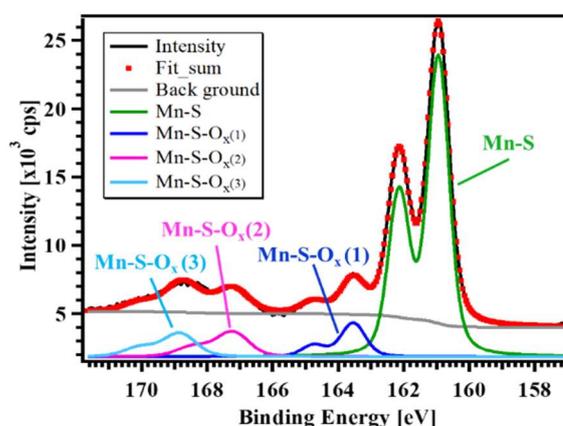


Fig. 3 S 2p spectral of MnS film deposited at 550 °C with 1.5 nm thick RT-MnS. Mn-S-O_x(1), (2), and (3) corresponds to valence states for Mn⁴⁺, 3⁺, and 2⁺, respectively

4. Conclusion

The thin film growth of MnS deposited by RF-magnetron sputtering method on the Si(100) substrate was investigated. The 4 °-off Si(100) substrate and the thickness optimization of RT-MnS improved the crystallinity and surface roughness of the MnS film. XPS measurements also revealed the Mn-S bonds deposited RF-magnetron sputtering were thermally stable at the film growth temperature of AlN.

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