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Stabilization of wurtzite $Sc_{0.4}Al_{0.6}N$ in pseudomorphic epitaxial $Sc_xAl_{1-x}N/In_yAl_{1-y}N$ superlattices

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Abstract—Pseudomorphic stabilization in wurtzite $Sc_xAl_{1-x}N$/AlN and $Sc_xAl_{1-x}N/In_yAl_{1-y}N$ superlattices ($x = 0.2$, 0.3, and 0.4; $y = 0.2$–0.72), grown by reactive magnetron sputter epitaxy was investigated. X-ray diffraction and transmission electron microscopy show that in $Sc_xAl_{1-x}N$/AlN superlattices the compressive biaxial stresses due to positive lattice mismatch in $Sc_{0.3}Al_{0.7}N$ and $Sc_{0.4}Al_{0.6}N$ lead to the loss of epitaxy, although the structure remains layered. For the negative lattice mismatched In-rich $Sc_xAl_{1-x}N/In_yAl_{1-y}N$ superlattices, a tensile biaxial stress promotes the stabilization of wurtzite $Sc_xAl_{1-x}N$ even for the highest investigated concentration $x = 0.4$. *Ab initio* calculations with fixed in-plane lattice parameters show a reduction in mixing energy for wurtzite $Sc_xAl_{1-x}N$ under tensile stress when $x \geqslant 0.375$ and corroborate the experimental results.

Keywords: *Ab initio* calculations; Sputter deposition; Nitrides; Superlattice; Metastable phases

1. Introduction

Metastable wurtzite scandium aluminum nitride ($Sc_xAl_{1-x}N$) alloys have attracted a lot of attention recently. A 400% increase in piezoelectric response for $x = 0.43$ [1] as well as an improved electromechanical coupling (k_t^2) [2–5] make this material a potential alternative to the commonly used pure AlN in telecommunication industry [6]. The anomalously large piezoelectric modulus d_{33} of $Sc_xAl_{1-x}N$ was proposed to be related to softening of the material caused by a competition between Sc and Al atoms for the bonding coordination of nitrogen, due to a metastable layered hexagonal phase of ScN [7]. Mixing enthalpy calculations indicate that wurtzite phase is favored up to $x = 0.55$–0.56 [8,9]. This suggests that further improvement in application-relevant material properties would be possible by increasing the Sc concentration. However, experimental studies show a driving force for promoting phase separation into more stable wurtzite AlN and cubic rock-salt ScN at elevated growth temperatures and Sc concentration $x \geqslant 0.3$ [10]. Band gap energy measurements indicate a structural instability around $x = 0.2$, leading to rock-salt ScN grains within $Sc_xAl_{1-x}N$ matrix in samples deposited at 850 °C [11].

Our previous *ab initio* theoretical study of ternary group IIIA–IIIB nitrides shows that the energy minimum in the potential-energy landscape shifts toward lower c/a values [12]. Furthermore, a general volume matching argument has been introduced to select alloying elements for giant piezoelectric response [12]. The in-plane lattice parameter a increases due to larger atomic volume of ScN as compared to AlN, leading to distortions in bond angle β [11,13], thus changing the c/a ratio. It has been theoretically predicted that epitaxial stabilization of $Sc_xAl_{1-x}N$ up to $x = 0.4$ could hinder the material disintegration through spinodal decomposition [8]. However, phase separation through nucleation and growth of semicoherent wurtzite AlN phases in domain boundaries of cubic ScN has been demonstrated during annealing of cubic solid solutions [14] and might be a limiting factor for alloy formation during thin film growth.

Ab initio calculations show that the structural properties of ScN in GaN/ScN and InN/ScN superlattices with overall Sc concentration less than 50% are closer to wurtzite than the layered hexagonal phase [15]. Additionally, the epitaxial stabilization approach was successfully utilized

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to stabilize cubic AlN in a TiN/AlN superlattice [16,17]. Recently, this technique was also used to stabilize cubic $Sc_xAl_{1-x}N$ in sandwiched TiN/$Sc_xAl_{1-x}N$/TiN *structures* with up to $x = 0.82$, and subsequently – in cubic TiN/(Al,Sc)N multilayers [18,19]. Theoretical critical thickness calculations of $Sc_xAl_{1-x}N$ in $Sc_xAl_{1-x}N$/AlN and $Sc_xAl_{1-x}N$/GaN heteroepitaxial systems using an energy balance model show that the critical thickness can vary between 2 nm and infinity, depending on lattice mismatch [20]. Highest critical thickness values were obtained for lattice matched $Sc_{0.18}Al_{0.82}N$/GaN, however, it should be noted, that kinetic limitations and other processes occurring during growth can allow thicker layers to be deposited, and that even small changes in the in-plane lattice parameters contribute to large uncertainties in these calculations. Also, the non-existent metastable ScN phases were not taken into account. Here we use epitaxial superlattice structures to explore the pseudomorphic (epitaxial) stabilization of wurtzite $Sc_xAl_{1-x}N$ with up to $x = 0.4$.

The effects of the stress, induced by different stabilizing layers, on the nucleation and phase stability of $Sc_xAl_{1-x}N$ ($x = 0.2$, 0.3, 0.4) can be investigated by introducing zero, positive, and negative in-plane lattice mismatch, thus influencing the nominal c/a ratio in ideally strained epitaxial $Sc_xAl_{1-x}N$ layers. For this purpose, three types of epitaxial superlattice structures were produced: (1) $Sc_xAl_{1-x}N$/AlN, where the $Sc_xAl_{1-x}N$ layers are subjected to compressive stress due to a larger in-plane lattice parameter as compared to wurtzite AlN; (2) nearly lattice matched $Sc_xAl_{1-x}N$/$In_yAl_{1-y}N$, where the In concentration was tuned to match $Sc_xAl_{1-x}N$ in-plane; and (3) $Sc_xAl_{1-x}N$/In-rich $In_yAl_{1-y}N$, where $Sc_xAl_{1-x}N$ layers experience biaxial tensile stress due to smaller in-plane lattice parameter compared to $In_yAl_{1-y}N$. In addition, *ab initio* mixing enthalpy calculations within the density functional theory (DFT) [21] framework were carried out to investigate the effect of different stress states on stability of wurtzite and layered hexagonal $Sc_xAl_{1-x}N$ with respect to phase separation, caused by different fixed values of the in-plane lattice parameter.

Strain is typically present in the films due to stresses caused by lattice mismatch between the layers. The more Sc is incorporated in the $Sc_xAl_{1-x}N$/AlN superlattice, the larger the lattice mismatch becomes, laterally compressing the $Sc_xAl_{1-x}N$ layers more and more if non-relaxed epitaxy is sustained. On the other hand, if the in-plane lattice parameter of $In_yAl_{1-y}N$ is tuned [22], lattice match to $Sc_xAl_{1-x}N$ can be achieved, or, in the case of In-rich $In_yAl_{1-y}N$, tensile biaxial stress can be induced in $Sc_xAl_{1-x}N$ during the initial stages of the growth. However, as the individual stress and strain states in the $Sc_xAl_{1-x}N$ layers are unknown, we will refer only to the lattice mismatch further on.

2. Experimental details

A series of samples with varying Sc concentration and different superlattice periods was prepared onto $Al_2O_3(0001)$ substrates at heater temperatures T_H of 500–700 °C in a ultra high vacuum (UHV) deposition system with a base pressure of 4×10^{-6} Pa. Magnetically unbalanced reactive DC magnetron sputtering in Ar/N_2 gas mixture (99.999999% pure) at a total process pressure of 0.66 Pa was performed. Separate elemental targets of In (99.995% pure), Al (99.9995% pure), and Sc (99.99% pure) were used in a constant power mode.

The $Al_2O_3(0001)$ substrates were ultrasonically cleaned in trichloroethylene, acetone, and isopropanol, as well as blown dry with N_2 prior to placing them in the growth chamber through a load-lock system. After thermal degassing at the selected T_H for 1 h, Al and Sc targets were clean-sputtered in Argon for 5 min before starting the deposition. $Sc_xAl_{1-x}N$/AlN superlattices were deposited on 50 nm thick high temperature (HT) AlN(0001) seed layers. Cubic HT ScN(111) with $d_{\{110\}} = 3.18$ Å was used as a seed layer in the case of $Sc_xAl_{1-x}N$/$In_yAl_{1-y}N$ due to closer in-plane lattice match to $In_yAl_{1-y}N$ in comparison to wurtzite AlN $a = 3.11$ Å. Also, during growth of $Sc_xAl_{1-x}N$/$In_yAl_{1-y}N$, a negative potential of 15 V was applied to the substrate to enhance the ad-atom mobility [23,24].

X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements of separately grown thin films of AlN, $In_yAl_{1-y}N$ and $Sc_xAl_{1-x}N$ were performed to estimate the growth rate as well as the composition. The magnetron powers were later adjusted to produce superlattice samples with $x = 0.2$, 0.3, and 0.4 in $Sc_xAl_{1-x}N$ layers with periods $\Lambda = 8$ and 16 nm. Total superlattice thickness was kept constant at 240 nm, while the number of periods was varied between 15 and 30 for $\Lambda = 16$ and $\Lambda = 8$ nm, respectively. $In_yAl_{1-y}N$ in-plane lattice constants were obtained using Vegard's rule, based on a study of magnetron sputtered InN by Hsiao et al. [22]. Concentrations x and y were chosen such that the in-plane lattice mismatch $\delta = (a_{ScAlN} - a_{InAlN})/a_{InAlN}$ varied from −3% to +7% throughout the deposition series. A list of grown superlattice samples, showing the nominal compositions, estimated in-plane lattice parameters, and lattice mismatch values, can be found in Table 1.

XRD for phase analysis and superlattice characterization and XRR measurements were done with a Philips Bragg–Brentano diffractometer in the $\theta/2\theta$ mode. Average in-plane lattice parameters were investigated by reciprocal space mapping (RSM) of the $10\bar{1}5$ reflection using a Philips X'Pert MRD diffractometer in low-resolution mode. Microstructural analysis was performed using a Tecnai TF20 UT FEG transmission electron microscope (TEM) operated at 200 kV. Cross-sectional electron transparent samples were prepared by mechanical cutting and polishing, followed by Ar^+ ion milling. Scanning TEM (STEM) and energy dispersive X-ray spectroscopy (EDX) maps were acquired using a ~1 nm^2 probe size.

The $Sc_xAl_{1-x}N$ alloys were modeled at compositions $x = 0.125$, 0.25, 0.375, and 0.5, according to the special quasirandom structure (SQS) [25] method using 128 atom supercells. In the simulations the projected augmented wave (PAW) [26] method implemented in the Vienna *Ab initio* Simulation Package (VASP) [27,28] was used with Perdew, Burke, Ernzerhof generalized gradient approximation (PBE-GGA) [29] for the exchange–correlation functional. We applied a $3 \times 3 \times 3$ Monkhorst–Pack [30] k-mesh and an energy cutoff of 400 eV in all calculations. Fixed in-plane lattice parameters $a_0 = 3.1318$ Å, 3.2884 Å, 3.4450 Å, and 3.6227 Å were used. The lowest one corresponds to the in-plane lattice parameter of wurtzite AlN ($\delta > 0$), the second and the third are an additional 5% ($\delta = 0$) and 10% ($\delta < 0$) increase, and the largest one corresponds to wurtzite InN. For these parameters, we calculate the total energy of the wurtzite (B4), layered-hexagonal (B_k), and cubic rock-salt (B1) phases of ScN and AlN, to see which phases are favored at different in-plane lattice parameters. To have the most relevant comparison between the B1 phase and the hexagonal phases, a B1 based supercell