Realization of Non-Polar Wurtzite AlN Films by Fe Substitution and Elimination

We have developed a new technique to synthesize non-polar wurtzite aluminum nitride (AlN)-based polycrystal-like films on various substrates, including glass substrates. It is a two-step procedure: the first step is to grow AlN films in which Fe substitutes more than 10% of Al sites, and the second is to eliminate Fe from Al sites by annealing. X-ray absorption near-edge structure analyses were used to reveal the chemical states of Fe through the procedure.

Wurtzite AlN is a wide- and direct-band-gap semiconductor that is a promising material for deep-ultraviolet (DUV) light-emitting diodes (LEDs) [1]. As the energy of DUV light is high enough to kill viruses and decompose toxic molecules, it is useful in the fields of medicine and healthcare. At present, mercury lamps and metal halide lamps are used as DUV light sources, but these require a significant amount of power, have a short life-span and are large. Therefore, there have been accelerating global efforts to design and develop DUV-LEDs to replace these lamps with LED systems that are energy-saving, long-lasting, and small.

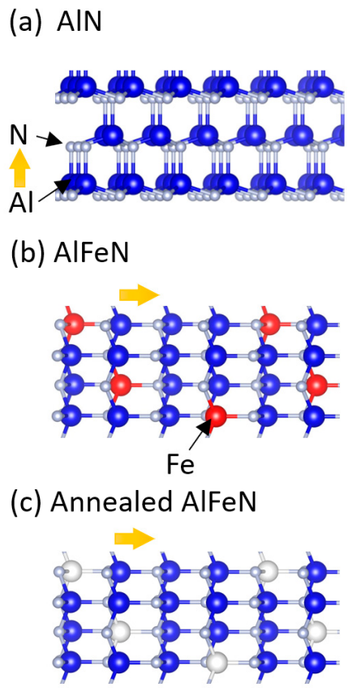

Figure 1: Schematic diagrams of polar and non-polar AlN films. The yellow arrows indicate the *c*-axis direction. **(a)** Al and N atoms form vertical arrays in wurtzite AlN films (polar orientation). **(b)** AlFeN films (Fe>10%) show non-polar axis orientation. **(c)** Annealed AlFeN films keep the non-polar axis-orientation.

Recently, however, it was found that AlN and related materials have challenging issues for high-efficiency LEDs. This is due to the electronic properties of thin films, which can be traced back to the crystal axis orientation of AlN, i.e. the polar-axis orientation [see **Fig. 1(a)**] [2-4]. Therefore, nonpolar-axis oriented AlN films which can avoid these problems have attracted much interest.

In 2018, we succeeded in growing non-polar-axis-oriented wurtzite films by heavy doping of Fe in AlN films [5]. The Fe-doped AlN (AlFeN) films were grown reproducibly on various substrates such as SiO_2 glass, Si and Al_2O_3(0001) substrates by sputtering. In the present study [6], to reveal the local crystallographic and electronic structures of Fe in AlFeN films, Fe *K*-edge X-ray absorption near-edge structure (XANES) measurements were conducted at the BL-9A beamline in fluorescence-detection mode. A comparison of the main edge energies of Fe in AlFeN film (Fe: 1.6%) and standard materials such as Fe metal (0), FeO (II), and FeN (III) was made [7]. The results suggested that Fe in AlFeN films has an oxidation state close to 3+ [6]. A pre-edge peak was observed in the AlFeN film spectra, similar to FeN where a Fe atom is surrounded by four nitrogen atoms with the non-centrosymmetric condition of the zincblende structure. This finding suggests that most of the Fe atoms in the AlFeN film occupy a site with non-centrosymmetric conditions, suggesting that Fe atoms in the AlFeN film occupy the Al sites of a wurtzite structure [**Fig. 1(b)**]. **Figure 2** shows the Fe *K*-edge XANES spectra of AlFeN films with various Fe concentrations when the electric field vector *E* of the incident X-rays was perpendicular to the film-plane. In the concentration range of Fe from 1.6% (*c*-axis orientation) and 19.9% (*a*-axis orientation), the main absorption edge energies and the existence of pre-edge peaks did not show a dependency on the Fe concentration. These results suggest that the Fe atoms in the AlFeN films occupy the Al sites of a wurtzite structure, irrespective of the orientation of the film.

In our previous study, it was shown that 3*d*-transition metals (3*d*TM) such as Ti [8], V [9], Cr [10] and Mn [11] create gap states in the gap of AlN when the 3*d*TMs occupy the Al sites, resulting in visible light absorption. Such gap states cause low efficiency of light emission via traps of carriers and reabsorption of emitted UV light in LED devices. In fact, N *K*-edge XANES spectra of the AlFeN films exhibit significant pre-edge peaks, which imply that electron unoccupied states are formed via Fe-*d* and N-*p* hybridization [6]. To remove the gap states, in other words, to eliminate Fe from Al sites, we annealed the AlFeN films under N_2 gas flow at various temperatures up to 1200°C. Fe *K*-edge XANES analyses imply that Fe atoms escaped the lattice sites and were oxidized near the surface during the long annealing time [6]. N *K*-edge XANES analyses also suggest a drastic decrease of the gap states while maintaining the non-polar axis orientation [**Fig. 1(c)**] by annealing. The origin of the preferred orientation change from *c*- to *a*-axis is still an open question. The behavior of Fe during annealing also remains to be clarified. In conjunction with the Fe concentration dependence of the extended X-ray absorption fine structure analyses, in-situ XANES analyses might reveal such behavior.

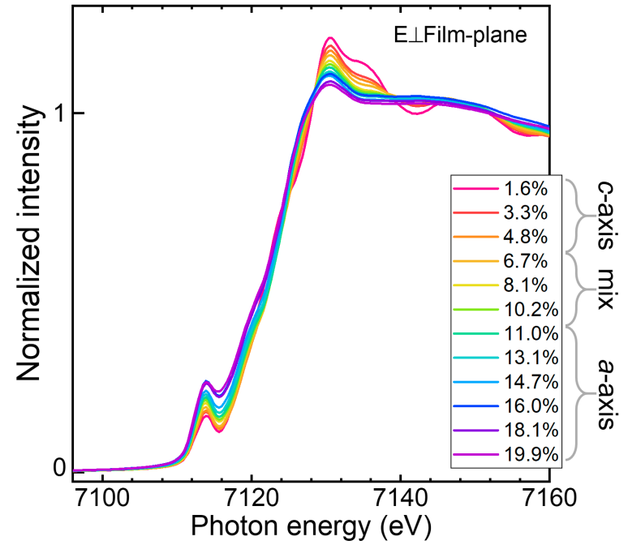

Figure 2: Fe concentration dependence of Fe *K*-edge XANES spectra of AlFeN in *E*⊥film-plane.

This new technique of heavy Fe-doping and post-annealing could be used to supply seed layers to construct non-polar AlN-based DUV-LEDs without expensive substrates or machines. Currently, the layers are polycrystal-like films. However, we plan to complete a higher quality seed layer to realize high-efficiency DUV-LEDs at low cost in the future.

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