

Origin of the Blue-Green Light Absorption of Ti-Doped AlN Films

We investigated heavily Ti-doped AlN films that absorb blue-green light. X-ray diffraction, transmission electron microscopy, and Ti *K*-edge X-ray absorption fine structure results revealed that most of the Ti atoms occupied Al sites of wurtzite AlN. *Ab initio* calculations revealed that the Ti-driven states were formed just below the bottom of the conduction band of AlN. The results of N *K*-edge X-ray absorption near-edge structure and X-ray photoionization spectroscopy supported the calculation results. Photoelectron yield spectroscopy results implied that the valence and conduction bands of the Ti-doped AlN meet the prerequisites for hydrogen gas production via photoelectrochemical water splitting.

For efficient photoelectrochemical splitting of water for the production of hydrogen gas, various attempts have been made to tune both the band gap energy (E_g) and the band edge potential in existing semiconducting materials [1]. Recently, group III-nitrides such as GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ have gained attention as promising materials because the well-understood band gap engineering technology can be used for preparing visible light driven photoelectrochemical cells [2-4]. However, $\text{In}_x\text{Ga}_{1-x}\text{N}$ with E_g of the visible light region encounter the problem that the conduction band (CB) minimum falls below the potential to produce H_2 from H^+ ions.

Heavy 3*d*-transition metal (TM) doping changes the band structure of III-nitrides: some 3*d*-TM doped III-nitrides show sub-band gap absorption with high absorption coefficient $>10^3/\text{cm}^2$ [5, 6]. Exploring the possibility of heavy 3*d*-TM doping of III-nitrides to confer photoelectrochemical activity under visible light, we have previously synthesized various 3*d*-TM doped AlN films and investigated their band structures [7-10]. Here we show the representative results of Ti-doped AlN (AlTiN, Ti

concentration up to 11%) that absorbs blue-green light accompanied with photoconductivity [10].

AlTiN films were deposited on an SiO_2 glass substrate by radio-frequency sputtering. The films showed optical absorption with onset energy of 2.2 eV as shown in Fig. 1(a). The X-ray diffraction (XRD) and transmission electron microscopy (TEM) results revealed that the films had a *c*-axis oriented wurtzite structure the same as that of undoped AlN films [10]. The oxidation states of Ti were deduced as 3+/4+ by comparing the edge energies of Ti *K*-edge XANES for the AlTiN film and standard materials. A strong pre-edge absorption peak in XANES spectra was observed in the AlTiN film spectrum, indicating that the Ti in AlTiN is surrounded by N atoms with non-centrosymmetric conditions such as T_d and C_{3v} . The results of extended X-ray absorption fine structure analysis showed that the bond lengths in the two directions (the electric field vectors were parallel and perpendicular to the *c*-axis of wurtzite structure) were similar, which implies that the Ti could have T_d site symmetry.

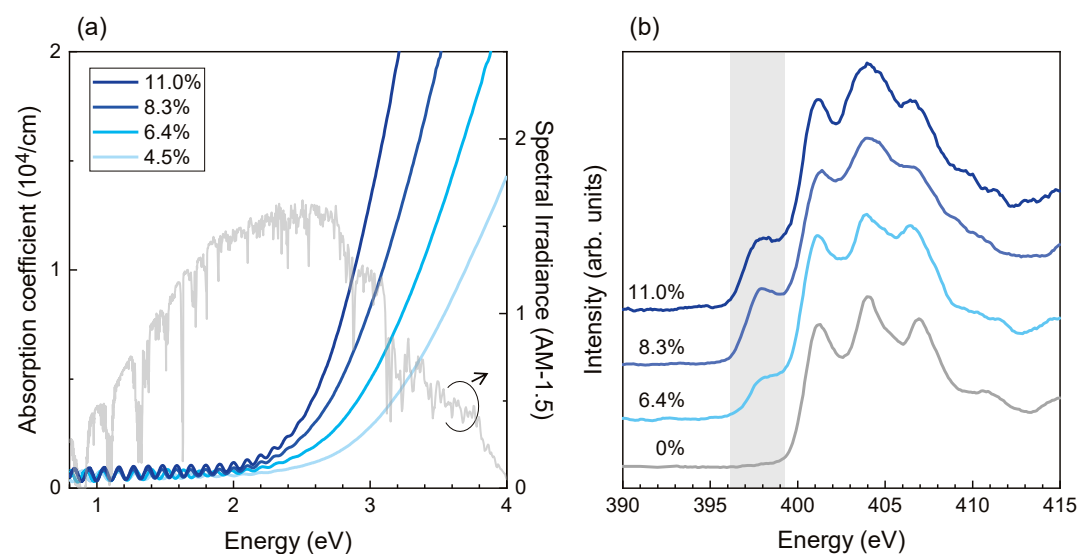


Figure 1: (a) Absorption coefficients (α) of AlTiN films with the solar spectral irradiance for air mass (AM) of 1.5. (b) N *K*-edge spectra of AlN and AlTiN. The thin gray zone is the pre-edge region.

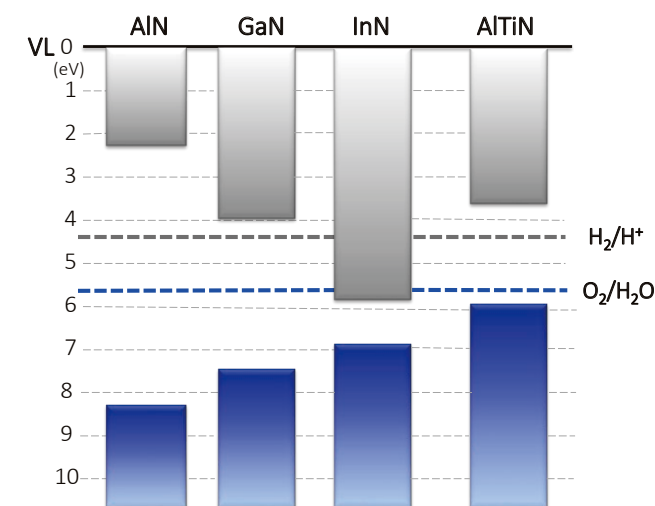


Figure 2: Band diagram for III-nitride and AlTiN with respect to vacuum level (VL). The gray bar is the CB and the blue bar is the VB. For AlN, the values were taken from ref. [12]. For GaN and InN, the values were taken from ref. [13]. The water oxidation and hydrogen reduction potentials are also indicated.

Ab initio calculations were conducted using lattice constants estimated from XRD data for supercells with Ti atoms occupying Al sites ($\text{Al}_{36-x}\text{Ti}_x\text{N}_{36}$, $x = 0-4$). It was revealed that the Ti-driven states were formed just below the bottom of the conduction band (CB) of AlN, and almost merged with it at high Ti concentrations. The calculated band structure was experimentally verified using X-ray photoemission spectroscopy (XPS) of the valence band (VB) region and N *K*-edge XANES. As representative data, the N *K*-edge XANES spectra of AlN and AlTiN films are shown in Fig. 1(b). The spectrum of AlN coincided with those previously reported for single crystals obtained experimentally and theoretically [11]. In the spectra of AlTiN films, an additional structure was observed in the pre-edge region. As N *K*-edge absorption is a transition from N 1*s* to unoccupied N 2*p* states, the additional structure implies the formation of unoccupied N 2*p* states just below the bottom of the CB with Ti-doping.

To investigate their band potentials, photoelectron yield spectroscopy (PYS) was carried out. In the PYS measurements, the excitation photon energy is swept and the photoelectron yield is obtained as a current flowing into the sample to compensate for photogenerated holes. The onset energy of photoelectron emission corresponds to the energy for electrons that are excited from the highest occupied electron state to the vacuum level (VL). For AlTiN films with high Ti concentrations, the onset energies were estimated at around 6.0 eV, indicating that the maximum of the VB lies at

around 6.0 eV as shown in Fig. 2. As the threshold energy of optical absorption was 2.2 eV, the minimum CB is thought to lie around 3.8 eV with respect to VL. These results indicate that AlTiN films can be used for water oxidation and hydrogen reduction.

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BEAMLINES

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