Characterization of a New Gate Insulator BN on InP Grown by Low-Temperature CVD

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A new gate insulator film, phosphorus-doped BN, has successfully been formed onto InP by low-temperature CVD. The results of XPS, AES and conductivity measurements have shown that a stable and comparatively stoichiometric BN film with high resistivity was obtained even at low temperatures (300-600°C) by using the two temperature zone technique. The density of interface states for the BN/InP system has been found to be comparable to that for the Si-SiO₂ system.

§1. Introduction

Considerable interest has recently been expressed in various technology developments for insulator formation onto InP, in order to apply them to high speed InP metal-insulator-semiconductor field effect transistors (MISFETs). However, no insulator-semiconductor system has so far been found in InP with as good qualities of dielectric and interface characteristics for electrical conduction as that in silicon. Therefore, more extensive investigations are now being requested in order to establish the technology for insulator film formation onto InP.

The present report has demonstrated high resistivity III-V insulator BN films grown by low-temperature chemical vapor deposition (CVD) onto InP. In order to investigate the applicability of BN to a gate insulator for InP, characteristics of the deposited BN films have been investigated using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and conductivity measurements. Properties of InP/BN interface have also been studied with the high frequency capacitance method and the conductance method.

![Figure 1: CVD equipment for the present experiment](image_url)
§2. Experiments

Figure 1 shows the CVD equipment. As shown in this figure, deposition was carried out using the two temperature zone technique with reactions of $B_2H_6$, $NH_3$ and $PH_3$. Namely, n-type InP wafers with a $2 \times 10^{16}$ cm$^{-3}$ carrier concentration were located in a low temperature zone of a quartz tube (deposition temperature $T_D = 300$-$600^\circ$C) in order not to cause surface degradation in InP. On the other hand, two source gases, $NH_3$ and $PH_3$ (5% in $H_2$), are heated up to 800$^\circ$C, just before the reaction, in order to make $N$ and $P$ atoms reactive. Then, this technique prevented both the formation of intermediate complexes and the volatilization of P atoms at the InP surface. Another source gas $B_2H_6$ (5% in $H_2$) was directly introduced into the sample zone without going through the high temperature zone, because preliminary experiments have shown that $B_2H_6$ gas became decomposed above 750$^\circ$C.

Every CVD film obtained in the present experiment was colorless and transparent, and was not attacked by all aqueous acids and boiling water. On the other hand, use of $N_2$ base gases yielded a BN film soluble in water. This is considered to be because the presence of residual bonded hydrogen is associated with BN film resistance to water attack$^2$.

§3. Results and discussions

3.1. Spectroscopy

Properties of chemical compositions for the deposited film were analysed by XPS and AES. Figure 2 shows the XPS results for various $T_D$ samples, where the sample surfaces were sputter-etched with Ar ion (5x10$^{-5}$ Torr with 20mA) at 3kV for 50-100sec in order to remove boron oxide layers within about 10nm. As shown in this figure, the spectrum was sensitive to the deposition temperature: In the signals assigned to $2p$-electrons for P atoms, the peaks at 130.0eV and 129.0eV, which correspond to the elemental phosphorus and to BP respectively, disappeared as $T_D$ increased. Furthermore, a strong chemical shift was observed from 188.3eV toward 191.0eV in $1s$-electron binding energy for B atoms as $T_D$ increased, while no chemical shift was shown in $1s$-electron binding energy for N atoms. Note that the N to B intensity ratio increased with increase in $T_D$. Quantitative analyses have shown that the CVD films approached stoichiometric BN as $T_D$ increased. It is also seen that, at any $T_D$, the spectrum for B had no peak at 187.0eV, which proved the existence of elemental boron.

The AES results showed the same behaviour for chemical shifts, as illustrated in Fig.3. Namely, the peak for N(KLL) signal showed no chemical

![Fig.2. X-ray photoelectron spectra for various $T_D$ samples.](image1)

![Fig.3. Auger electron spectra for various $T_D$ samples.](image2)
shift, while a strong chemical shift from 179eV toward 172eV was observed for the B(KLL) signal as $T_D$ increased. Further, it is shown that, at $T_D=570°C$, the B(KLL) signal had another peak at 182eV. The peak-to-peak amplitude ratio of N(KLI) to B(CIT) was also found to increase with an increase in $T_D$.

3.2. Conductivity

Electrical transport properties for the deposited insulators were studied by measuring current-voltage characteristics. Figure 4 shows the results of conductivity $\sigma$ versus square root of electric field $E$ for various $T_D$ samples at room temperature. Here, every datum was for the gate electrode positive (semiconductor accumulate) in Au/BN/n-InP MIS diodes. It is clearly seen from this figure that the current transport in the CVI) films can be well explained by the Poole-Frenkel mechanism in high electric fields. Dynamic dielectric constant, $k_{op}$, which was obtained from the slope in Fig.4, was found to be 2.94 for every $T_D$. This value is consistent with the result of refractive index $n$ at 633nm obtained from ellipsometry; $n^2$ is found to be 2.96 for the samples deposited at 300-600°C. Furthermore, the insulator breakdown field has been found to be more than 3x10^6V/cm.

At low fields, current versus voltage characteristics should behave in an ohmic manner. The conductivity in such ohmic regions, $\sigma_{ohm}$, can be estimated from extrapolation of $\sigma$ toward $E=0$, unless other transport mechanisms dominate the electrical conduction at low fields. It is shown in Fig.4 that the resistivity defined by $\sigma_{ohm}^{-1}$ is more than 10^{16}Ωcm and increases strongly as $T_D$ increases. This is believed to be because the chemical deposition at higher $T_D$ brought more stoichiometric BN insulators, as discussed before, which have larger barrier-height.

3.3. Interface states

Typical capacitance $C$ versus gate voltage $V_g$ characteristics are shown at various frequencies for an Au/BN/n-InP MIS diode ($T_D=570°C$) in the inset in Fig.5, where the insulator thickness was 1070A and the gate electrode had a 1.1x10^{-3}cm² area. It is shown in this figure that the frequency dispersion of accumulation capacitance was very small. In Fig.5, this frequency
dispersion is shown for various $T_D$ values, where $C(f)/C(1\text{MHz})=1$ at 10V was plotted as a function of frequency $f$. This clearly indicates that the frequency dispersion of accumulation capacitance decreased as $T_D$ decreased and was less than about 2.5% even for $T_D=560^\circ$C. This result makes the estimation of insulator capacitance and resultant density of interface states, using the high frequency capacitance method, much less erroneous.

From the data for insulator capacitance at 1MHz, the static dielectric constant $\kappa_i$ was estimated to be 5.75±0.28 for any $T_D$ sample. This $\kappa_i$ value is rather larger than that for boron-rich films reported by Rand and Roberts $^2$ ($\kappa_i=3.7$) and agrees well with that for polycrystalline BN reported by Hyde and Yep $^4$ ($\kappa_i=5.3-7.7$).

Figure 6 shows the results for density distribution of interface states, obtained using the high frequency capacitance method (C-V) and the conductance method (G-ω). It is shown in this figure that the chemical deposition at $T_D$ around 430°C gave very small density of interface states near the midgap. The value was about 1×10$^{10}$ cm$^{-2}$eV$^{-1}$ or less, and is comparable to that for an Si-SiO$_2$ system. The density of interface states has also been found to increase as $T_D$ increases above 500°C. This is believed to be due to the thermal degradation of InP surface.

§4. Conclusions

(1) Analyses of XPS and AES showed that stable and comparatively stoichiometric BN film was obtained, even at low temperatures ($T_D=400-600^\circ$C). Both peaks of XPS and AES signals for B atoms showed strong chemical shifts with changing B/N ratio.

(2) Resistivity for the CVD-BN film was more than 10$^{16}$ Ohm-cm, and the breakdown field was more than 3×10$^6$ V/cm. The insulator resistivity in ohmic regions increased with an increase in $T_D$, which was mainly caused by increasing the barrier-height due to approaching a more stoichiometric BN. The dynamic dielectric constant, deduced from the Poole-Frenkel conduction, was 2.94 for every $T_D$ and was consistent with the ellipsometry results.

(3) By using the data for accumulation capacitance at 1MHz in the BN/InP MIS diodes, the static dielectric constant could be estimated to be 5.75±0.28 for every $T_D$. The density of interface states shown U-shaped distribution, and became minimum around the midgap for the BN/InP system. The minimum value was about 10$^{10}$ cm$^{-2}$eV$^{-1}$ or less at $T_D=430^\circ$C. Thus, it can be concluded that the CVD-BN film is a suitable gate insulator for InP MIS devices.

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References