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Plasma-Deposited Boron Nitride as a New Class of Insulating Film

cubic (高圧型)
hexagonal (低圧型)
(高温-plasma)

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Insulating boron nitride films have been prepared by the glow discharge decomposition of NH_3+B_2H_6 at 300 °C, and the energy band diagram of a metal/BN/Si system has been quantitatively determined for the first time by the internal photoemission technique. The capacitance-voltage characteristics of the MIS structures exhibits no hysteresis and a small flat-band shift. The BN films are found to be thermally stable up to 800 °C. This dielectric material can be utilized as a new type of insulator for passivating semiconductor devices.

§1. Introduction

Stoichiometric boron nitride either with hexagonal structure or with cubic is thought to be an appropriate insulating material for passivating semiconductor devices or LSIs, because BN is highly insulating, chemically inert and thermally stable. BN thin films have so far been prepared either by CVD[1,2] or by high temperature reactive plasma,[3] and very preliminary characterization of the electronic properties have been attempted although definite values of the dielectric constant, refractive index and optical bandgap have not been obtained.[1,3] A wide range variation of the material constants mainly arises from the poor control of the stoichiometry of BN.

Recently we have reported that BN films can be produced at a temperature below 300 °C by the rf glow discharge decomposition of a B_2H_6+NH_3+H_2 gas mixture.[4] The optical bandgap and static dielectric constant of the deposited BN films have been determined to be 5.0 eV and 6.5, respectively. The surface state density in the BN/Si interface was fairly low compared with that in the plasma-deposited Si_3N_4/Si interface.

In this paper, we have determined the energy band diagram of a metal/BN/Si system using internal photoemission over the barrier. The result was fully consistent with the flat-band voltage measured from the capacitance-voltage characteristics. The dielectric properties and thermal stability of BN films are carefully examined. It is shown that BN is electrically and thermally stable and can be utilized as a new type of insulator for semiconductor device applications.

§2. Experimental

Stoichiometric BN films were deposited on Si substrates at a temperature below 300 °C using the rf glow discharge decomposition of a B_2H_6+NH_3+H_2 gas mixture. The deposition technique and apparatus have been described in detail elsewhere.[4,5] For the internal photoemission measurements, semitransparent Au or Al gates with ∿200 A in thickness and 2 mm in diameter were evaporated on BN, and the transmission coefficient of the deposited metal gates was calibrated by the optical absorption coefficient of the films simultaneously evaporated onto qurtz substrates. The monochromatic light in the energy range 3 - 6 eV for exciting photoelectrons was obtained by a combination of a high-pressure mercury arc lamp and a grating monochromator. Thermal stability of BN at temperatures between 300 °C and 800 °C was tested by annealing the film for an hour in a nitrogen gas atmosphere and then the infrared absorption spectrum and surface morphology were observed.

§3. Results and Discussion

The quantum yield Y_b for photoemission i_p is

given as a function of incident photon energy hν for a MIS system by the following equation:[6]

$$Y_b(h\nu,\Phi) = KN_f(\Phi)|M_{if}|^2 l(\Phi) \\ x[1+\alpha(h\nu)l(\Phi)]^{-1}(h\nu-\Phi)^3. \quad (1)$$

Here, K is the constant, N_f is the density of the final state, Φ is the barrier height or the threshold of photoemission, M_{if} is the matrix element for band-to-band transition, l is the mean-free length of the excited electrons, and α is the optical absorption coefficient. The measured photoemission current normalized with the incident photon flux density is proportional to $Y_b(h\nu,\Phi)$ in eq. (1).

In Figs. 1 and 2 the cube root of photoresponse is plotted against photon energy for Au and Al/BN/n-Si(100) structures. The curves at photon energies below 5 eV in Fig. 1 refer to the electron emission from the metal gates and hence the threshold energy corresponds to the onset of photoemission of electrons from the metal Fermi level to the bottom of the BN conduction band. The difference of the threshold energy for Au and Al gates is primarily due to the work function difference of the both metals, whose value is estimated to be 0.9 eV from the internal photoemission of Au and Al/SiO_2/Si structures and to be 0.55 eV from the vacuum work function difference.[7] The threshold energy for positive gate bias is independent of metal work function as shown in Fig. 2, because electron emission occurs from the top of the silicon valence band to the bottom of the BN conduction band.

The excess photocurrent observed in the photon energy range 2.2 - 3.5 eV in Fig. 2 is roughly proportional to photon energy. This implies that the photoemission takes place from electronic states of silicon distributed in a narrow energy range. Since the interface state density is not too high ($\sim 10^{11}$ $cm^{-2}eV^{-1}$) and the excess current is not observed when p+-Si substrates are used, it is likely that the excess photoresponse in Fig. 2 originates in the electron emission from the bottom of the Si conduction band, whose threshold is estimated to be ~2.0 eV from the figure. The sharp increase in the photoemission yield above 5.2 eV in Figs. 1 and 2 is attributable to the photocarriers generated by the band-to-band transition in BN, since the kink energy is independent of metal work function and of polarity of gate bias, and is close to the optical bandgap energy (5.0 eV) determined by the optical absorption measurment. As a consequence, the energy band diagram of a metal/BN/Si structure is derived as shown in Fig. 3. In the figure the zero-field barrier height Φ_0 is given by taking into account the image-force barrier lowering ΔΦ described as:

$$\Delta\Phi = \sqrt{qE/\pi\varepsilon_d}, \quad (2)$$

where E is the electric field strength in insulator and ε_d is the insulator dielectric constant. The value of Φ_0 is therefore obtained from the photoemission threshold Φ by noting the relationship $\Phi_0 = \Phi + \Delta\Phi$.

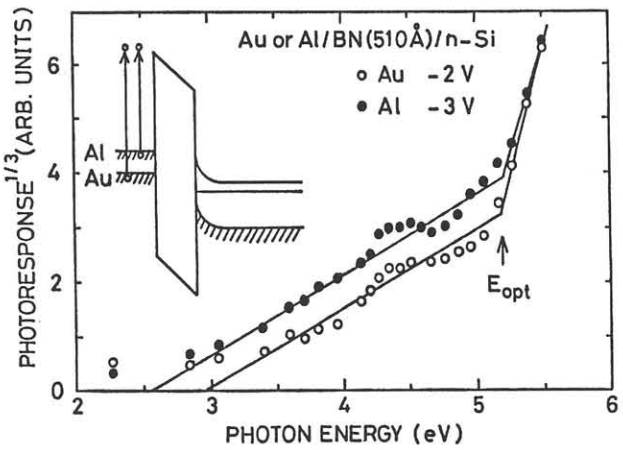

Fig. 1 Cube root of photoresponse as a function of photon energy for negatively biased MIS structures.

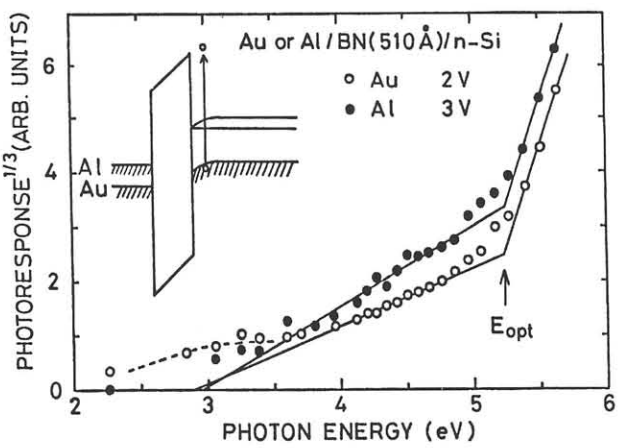

Fig. 2 Cube root of photoresponse as a function of photon energy for positively biased MIS structures.

The potential barrier at the BN/Si interface is 1.9 eV, which is in good agreement with the onset of the excess photocurrent due to photoemission from the Si conduction band as observed in Fig. 2. The work function difference between Au and Al in Fig. 3 is 0.4 eV, which is in consistence with the vacuum work functions of the both metals. This is also confirmed by the difference of the flat-band voltages for MIS structures with Au and Al gates (Fig. 4). The respective flat-band voltage shift estimated by the result of Fig. 3 is 0.8 V, which corresponds to a total charge density of 5.6×10^{11} cm^{-2}. Note that there is no hysteresis in the C-V curves of Fig. 4 and the interface state density calculated by the quasi-static C-V characteristics is as low as 1×10^{11} $cm^{-2}eV^{-1}$ near midgap. Fairly low density of interface states and absence of C-V hysteresis in the BN/Si system is considerably different from the properties of the Si_3N_4/Si system.[8]

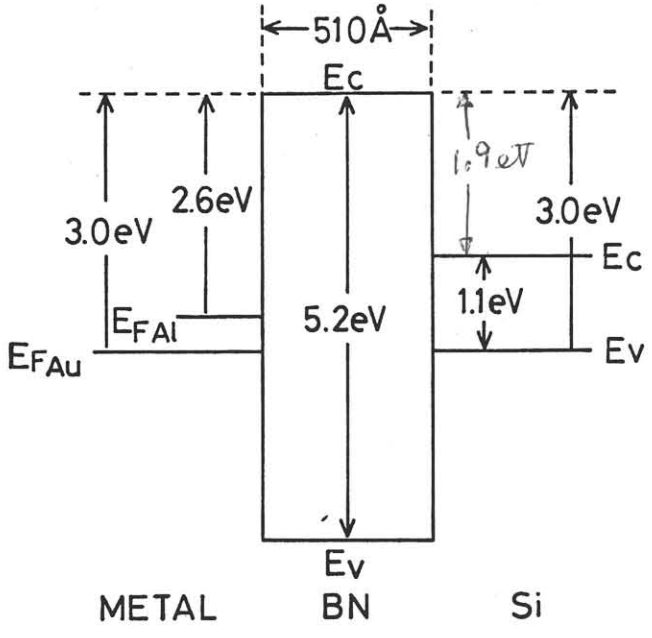

Fig. 3 Energy band diagram for a metal/BN/Si structures.

The current-voltage characteristic of a MIS structure exhibits the Poole-Frenkel conduction at high electric fields as shown in Fig. 5 and the dynamic dielectric constant obtained from the plot was 5.8 which is compatible with the static and optical dielectric constants (Table I).

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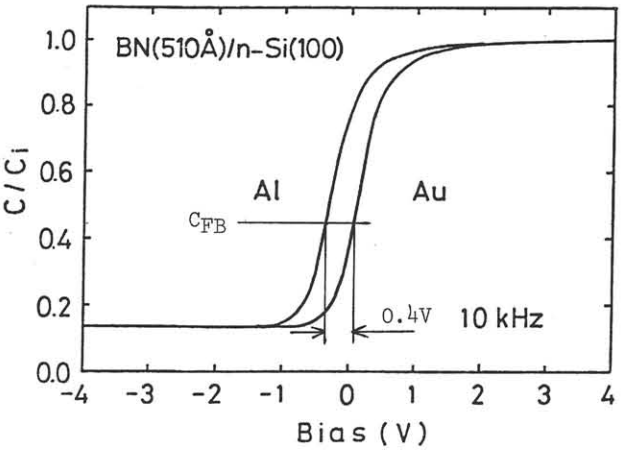

Fig. 4 Capacitance-voltage curves of MIS structures with Au and Al electrodes.

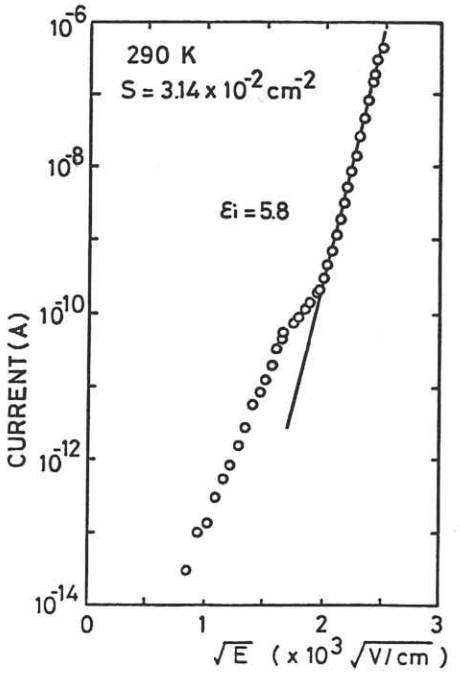

Fig. 5 Current-voltage characteristic of an Al/BN (330 A)/Si diode.

Table I. Fundamental properties of BN films

breakdown field	static dielectric constant	dynamic dielectric constant	optical dielectric constant
> 3 MV/cm	6.5	5.8	3.1

5.7~7.1

Thermal stability of BN films prepared at a temperature of 300 °C was studied by measuring annealing effect of the vibrational absorption intensity due to the NH stretching mode (Fig. 6). The amount of NH bonds incorporated in the BN network was almost unchanged even by annealing at 600 °C, being decreased to about 65 % of those of an as-grown sample by annealing at 800 °C because some of the bonded hydrogen is thermally effused. The infrared absorption due to the BH stretching mode at 2510 cm^{-1} is absent in the as-grown network. The vibrational absorption due to the BN lattice mode at 1370 cm^{-1} and 800 cm^{-1} was completely unchanged by annealing at 800 °C. Furthermore, it was shown that the surface morphology observed by SEM was kept identical up to 800 °C annealing.

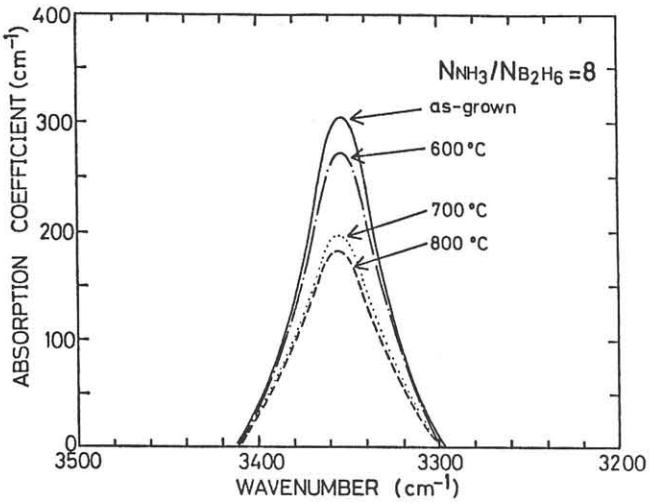

Fig. 6 Infrared absorption coefficient for the NH bonds measured after each annealing step.

§4. Conculution

The energy band diagram for a metal/BN/Si system has definitely been determined by the internal photoemission technique. The BN/Si barrier height is high enough to block the thermal carriers in Si. BN films are found to be thermally stable up to 800 °C annealing.

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C-V ヒステリシスはあり。
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Native Oxideの影響もあり