Comparison of optical and electrical properties of BON and Ti-BON thin films prepared by PAMOCVD method

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Abstract

We have firstly grown the BON and Ti-BON thin films on Si(100) in the deposition temperature range RT ~ 500 °C by low frequency radio frequency derived plasma assisted metal organic chemical vapor deposition. Trimethylborate and tetrakis dimethyl amino titanium precursors were used to grow BON and Ti-BON thin films. N₂ gas as additional nitrogen source was used for reactive gas and the plasma source gas was Ar. Comparative studies of electrical and optical properties between BON thin film and Ti-BON thin film were mainly investigated in this study. FT-IR results show that the bond type in the films is very similar to B–O–N and prefer to angular structure rather than linear one. UV/Vis results show that BON is semiconductor material with 3.4 eV of wide band-gap, and PL results show that the optical band-gap is 3.5 eV. It means that the conduction band-gap is less than the optical band-gap. Thus, the BON film gained in this case was a band-structured material with heavy doping. In terms of the I–V curve and film thickness, the electric conductivity is deduced as $8 \times 10^{-2} \, (\Omega \cdot \text{cm})^{-1}$, which is as same order-magnitude as $4.3 \times 10^{-2} \, (\Omega \cdot \text{cm})^{-1}$ measured by four-points probe method. This means that the BON thin films could have a semiconductor nature. Similar results as BON were also obtained from Ti-BON thin films grown under the same deposition condition. However, we found that electrical and optical properties of the as-grown Ti-BON thin films were strongly dependent by nitrogen flux and growth time. Typically, the electrical resistance was decreased with increasing the nitrogen flux and growth time. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: BON and Ti-BON thin films; Low frequency RF-PAMOCVD; Optical and electrical properties

1. Introduction

In the past years, the Ti–B–N, Ti–B–O and Ti–B–C [1,2] systems have been widely studied especially for its mechanical properties. But optical and electrical properties have not been studied widely.

Recently the nanocomposited materials, composed of boron (B) with other light elements such as nitrogen (N), carbon (C), oxygen (O), etc. are interesting, because of their excellent properties for insulation [3] and nonlinear optical behavior [4]. Thus, they are attractive for electronic devices and wide band-gap optoelectrical devices and laser devices [4]. Recently, the possibility of existence of BON material has been proposed [5]. So far, however, there was no report on the properties of BON material in detail. And we also synthesized Ti-BON thin films by a combination of trimethylborate (TMB) precursor and tetrakis dimethyl amino titanium (TDMAT) precursor, expecting that the titanium component can enhance the hardness of the film and shows a different optical/electrical properties compared to BON. Radio frequency (RF) plasma assisted metal organic chemical vapor deposition (MOCVD) has been applied to the fabrication of oxide [6], nitride [7] and boron-containing materials [8]. The frequency was usually 13.56 MHz in these cases. High rate of gas-phase dissociation was expected [9] by using such a high frequency that may be resulted in the multi-deposit fabrication of multi-element compounds. To avoid this disadvantage, a deposition process with low frequency is highly desirable. In this paper, therefore, we reported the fabrication of BON and Ti-BON thin films by low frequency (100–300 kHz) derived plasma assisted MOCVD, and mainly studied their optical and electrical properties with deposition parameters.

2. Experimental

The procedure of BON and Ti-BON fabrications was done in a set of parallel plate electrode discharged system. The plasma was derived by low frequency RF
in the range of 100–300 kHz frequency and 500 W of power. The plasma source gas was Ar in which the flux was 200 sccm. N2 gas was used in the range of 20–100 sccm flux. The TMB, (OCH3)2N, was used as boron, carbon and oxygen sources by a gas distribution ring with 2 sccm flux. TDMAT, [(CH3)2N]2Ti was used as titanium source by another gas distribution ring with 5 sccm flux. The general working pressure was 600 mTorr–2 Torr in the chamber. The substrates were one-side polished single crystalline silicon wafer with (1 0 0) crystal surface and micro cover glass. Before they were installed on the substrate heater in the deposition chamber, they underwent degreasing and drying in vacuum. The substrate temperature measured by Chromel–Alumel thermocouple was maintained in the range of room temperature to 500 °C. The longest deposition time was 5 h.

3. Results and discussion

Fig. 1 is the binding energies of B1s (a), O1s (b), N1s (c), C1s (d) of as-grown BON film obtained by the high resolution XPS. The binding energies of each element are 191.5 eV (B1s), 531.2 eV (O1s), 399.4 eV (N1s) and 284.4 eV (C1s), respectively. Since the binding energy of N1s is higher than 398.1 eV, attributing to direct bond between B and N atoms. N is more closely bonded to O rather than to B. On the other hand, the binding energies of O1s and B1s are also smaller than 533.24 and 193.70 eV, respectively. That means there is no B2O3 structure in the films [10]. However, the X-ray photoelectron survey spectra (not present here) showed that the carbon content decreased from 23 to 1% after the Ar ion sputtering. When the sputtering depth is less than 3 nm, the carbon is the adsorbed species on the BON surface. The reason for the raised carbon content on the surface is mainly due to the air contamination after the deposition. So, the main deposit in the film should be BON. The composition of the as-grown BON film at 500 °C with the N2 (20 sccm) plasma measured by XPS is B:O:N = 32%:42.1%:25.8%.

Fig. 2a is the FT-IR result obtained from the BON film grown on Si(1 0 0) substrate at 500 °C for 4 h. It shows that there is a broad and strong peak at 1580–1270 cm–1. The peak occurring at this range was regarded as graphite carbon structure, B–O and B–N, respectively. Based on the analysis of binding energies in Fig. 1, our film can have the B–O–N bond. So, the peak at 1351 cm–1 can be regarded as B–O–N feature vibration in IR spectra. Then the bond type in the films is very similar to B–O–N. It is well known that h-BN has two vibration frequencies at 1390 and 750 cm–1 [11]. In our case, B may not directly be bonded with N.
as mentioned above. One can imagine that the interaction between B and N is weaker than that in BN. So, the vibration due to this interaction will occur at lower energy range than that in the BN for IR spectra. Thus, we regard that the peak at 1351 cm$^{-1}$ shows the interaction between B and N with weak constant force compared to h-BN. In the case of Ti-BON thin film, the peak at 1345 cm$^{-1}$ in Fig. 2b show the shift of B–O–N vibration peak. The reason for shift is that the titanium content accepts electrons from the B–O–N bond so that the interaction between B and N is weaker than that in B–O–N. And the peak at 1965 cm$^{-1}$ shows the C–H vibration peak contributed to aliphatic carbon contents of titanium source, TDMAT. If BON is linear structure, the distance will be 3.85 Å ($R_{\text{oxygen}} = 0.61$ Å) which is approximately 3 times as long as the BN bond length according to the data in Ref. [12]. Such a long distance is impossible for B and N to form a strong enough interaction, and can not be detected by IR. So, we concluded that the atoms of B, O, N in the films prefer to angular structure rather than the linear one. From the XPS and IR data, the formation of BON bond is the result of nitrifying the B–O radical by activated nitrogen and the Ti-BON thin film has more carbon contaminant than BON thin film. This indicates that low frequency derived plasma is one of the available methods for material fabrication to utilize the former bond existence in the precursor.

The band-edge absorptions of BON and Ti-BON thin films grown on glass substrates were detected by Ultraviolet UV/Vis absorption spectra, shown in Fig. 3. With the decrease of nitrogen contents, the transmittance was reduced and the band-edge adsorption tends to have small wavelength in Fig. 3a. For example, the BON thin film with $N_2$ (60 sccm) does not have high transmittance ($\approx 50\%$) in the IR region, through the visible and into the UV regions, where it drops sharply due to the band edge of the material. With almost straight-line interception at approximately 360 nm wavelength, a band-gap of 3.4 eV is deduced. This result also can be found by photoluminescence exciting (PLE) in Fig. 4a. The absorption occurs at 354 nm. So, the ‘optical band-gap’ is 3.5 eV, which accords well with the UV results. The
Fig. 4. Typical PL spectra of (a) BON and (b) Ti-BON thin films.

PL occurs at 633 nm. It means that the conduction band-gap is less than the optical band-gap. Thus, the BON film gained in this case was a band-structured material with heavy doping. The electrical conductivity of the film was also measured by four-points probe method. The conductivity was $4.8 \times 10^{-2} \, \Omega^{-1} \cdot \text{cm}^{-1}$. This result suggests that the band-gap of BON can be tailored from insulation to semiconductor by the changes of the nitrogen and oxygen of BON in UV protection.

In the case of a typical Ti-BON thin film (Fig. 3b), the transmittance was reached up to 90% in the IR region and band-edge adsorption occurs at less wavelength than that of BON thin film. However, with the increase of nitrogen flux, the transmittance was reduced. Especially, the Ti-BON thin film with $N_2$ (60 sccm) does not have high transmittance ($\approx 60\%$) in the IR region. It is the reason for that Ti-BON thin film with $N_2$ (60 sccm) contains nanocrystals of TiN embedded in an amorphous matrix. We can confirm this result from XRD data (not present here). With the almost straight-line interception at approximately 285 nm wavelength, a band-gap of 4.37 eV is deduced. As a whole, the optical band-gap increased. Usually, the band-gap increases has a tendency for electrons to become more and more located to the atoms. That is why boron oxide and boron nitride are insulator. In our case, the nitrogen nitrifying Ti results in the tendency for electron to become located from oxygen. So, the band-gap becomes wide. This result can also be found by PLE in Fig. 4b. The absorption occurs at 326 nm. So, the ‘optical band-gap’ is 3.8 eV. The PL occurs at 663 nm. Generally, we can see the red shift rather than that of BON thin film.

The current–voltage feature was characterized on Al/ as-grown film/Si structure. Fig. 5a shows experimentally observed the forward-voltage vs. current curves of BON thin films. The curves a and b shows a typical Shottky barrier diode feature [13]. The difference between curves a and b is that the cut-in voltage is smaller in curve a than that in curve b. The curve c contains two steps. It seems to consist of two MS structures. The four-point probe method was used to measure the resistivity of as-grown films before $I-V$ characterization. The measured values are of 34.82, 22.22 and 20.53 ($\Omega \cdot \text{cm}^{-1}$) of sample a, sample b and sample c, respectively. This means that as-grown BON films have either insulator or semiconductor properties, depending on nitrogen contents in the films. Boron nitride and boron oxide are well known insulators. The band-gap of BN and B–O is 5.6 and 5.8 eV [14].

In our case, the incorporation of $N_2$ and N (especially N) into B–O radicals results in the change of insulator to semiconductor. Furthermore, the resistivity decreases
with the increase of N-content in the film. The possible reason may lie in that the electron localized near B–O bond is delocalized due to the join of N atom because the difference of electronegativity between N and O is less than a. Therefore, the band-gap becomes narrower than original state. With the increase of N-content in the films, the number of delocalized electrons increases, and then, the band-gap decreases further.

Otherwise, Fig. 5b shows the forward-voltage vs. current curves of Ti-BON thin films. Compared with that of BON thin film, the leakage current decreased as a whole and we can see the characteristics of insulator with the decrease of nitrogen contents in the films. The reason is that titanium is short of electrons. So titanium receives electrons from nitrogen. These results interfere with the delocalization of the electrons localized near B–O bond. However, we can slightly see two steps with the increase of nitrogen contents in the film just like that of BON thin film. The reason is that enough nitrogen contents can offset the existing effect of titanium contents. Consequently, Ti-BON thin film lies halfway between insulator and semiconductor and we can control the electrical properties from the adjustment of titanium and nitrogen contents. But the I–V characteristics of Ti-BON thin film shows less effect to nitrogen flux than that of BON thin film.

4. Conclusions

BON and Ti-BON thin films were fabricated by low frequency RF in the range of 100–300 kHz frequency derived plasma enhanced MOCVD method with TMB precursor and TDMAT precursors, respectively. The formation of BON was the result of nitrifying B–O radicals by nitrogen radicals, and formed angular molecular structure. BON and Ti-BON were band-structured materials with heavy doping. The BON thin film does not have high transmittance (~50%) in the IR region. The transmittance was reduced with the decrease of nitrogen flow late. The band-edge absorption tends to reduce wavelength. In the case of Ti-BON thin film, however, the transmittance was reached up to 90% in the IR region and band-edge absorption occurs at fewer wavelengths than that of BON thin film. In addition, we obtained that the as-grown BON thin film had the electrical properties of insulator to semiconductor, while Ti-BON thin film lies halfway between insulator and semiconductor.

References