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SIMS depth profiling of thin boron nitride insulating films

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Secondary ion mass spectrometry (SIMS) has been used to determine depth profiles of thin boron nitride films adapted as insulators in metal–insulator–semiconductor (MIS) devices. The negative secondary ion detection has been chosen to overcome the sample surface charging due to Ar^+ primary ion beam bombardment and to determine the elemental distribution without an electron flood gun treatment. Thin boron nitride films of 20–200 nm thickness were obtained by the radiofrequency plasma-assisted chemical vapour deposition method on Si-substrate with various flows of the gas source. The effect of silicon diffusion from the substrate into the insulator on nitrogen detection due to multiply charged Si ion mass interferences is observed. In order to entirely eliminate the silicon contribution to nitrogen signal in SIMS, we propose to produce BN film on two substrates (e.g., Si and GaAs) simultaneously and then to determine the nitrogen profile. The data obtained for MIS devices formed by covering the BN film with Al layer reveal also Al presence in the insulating film.

Key words: *SIMS; boron nitride; depth profiling; charging effects*

1. Introduction

Due to wide band gap, good chemical inertness, thermal stability and conductivity as well as enhanced hardness, cubic boron nitride (c-BN) is suitable for numerous potential applications. These cover such areas as high-temperature and high-power electronics, UV (including deep UV) detection, and light emitting devices or structures intended to work in chemically harsh environments [1–3]. However, recently the most promising applications of this material are wear resistant coatings and electrical insulation for metal–insulator–semiconductor (MIS) devices [4–6].

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In this paper, secondary ion mass spectrometry (SIMS) study is presented of thin insulating boron nitride films (20–200 nm thick), deposited on Si or GaAs substrates using the plasma method. However, the interpretation of SIMS data is not straightforward in the presence of surface contaminations and matrix effects in which the sputtered ion yield depends strongly on the local film chemistry. The picture is further complicated by a factor, characteristic of insulating materials, limiting the secondary ion emission (often the secondary ion signal is eliminated entirely; this is not the case here) induced by net electric field at the sample surface produced by charged beam bombarding. This effect strongly depends on the penetration depth of primary ions as well as on the resistivity of the investigated layer and its thickness.

The observed features of the SIMS profiles have been discussed in terms of common mass interferences, matrix dependence and charging of nonconductive films during Ar^+ beam sputtering. Boron, nitrogen and silicon depth profiling have been discussed in detail as well as distribution of contaminations in the examined structures. Investigations of the BN gate insulator of complete MIS devices, accomplished by covering the BN/Si structure with an Al-layer provide additional information on factors disturbing the depth profile due to aluminum and silicon diffusion into the BN film.

2. Experimental details

Boron nitride films were produced on p-type Si (conductivity σ = 6–8 Ω·cm) or monocrystalline GaAs <100> oriented substrates using the radio frequency (RF) plasma-assisted chemical vapour deposition (PACVD) method [7–9]. The substrates were used to test technological parameters of the boron nitride material. Insulating layers were synthesized from $(C_2H_5)_3B$ vapours carried by nitrogen (2 cm^3/min or 3 cm^3/min). Complete MIS devices with boron nitride playing the role of the insulator were obtained by means of vacuum evaporation of round Al gate electrodes (1 mm in diameter).

The thicknesses of the formed layers were evaluated by ellipsometry measurements and confirmed also by the sputtering rate and the depth of the eroded craters after SIMS analysis using a Tencor α-step 100 profilometer. The thicknesses of thin BN films were in the range of 20–200 nm, while those of the cover Al-layers were ca. 100–500 nm, depending on the evaporation time.

The SIMS measurements have been performed using an SAJW-05 instrument with a low energy (5 keV) Ar^+ beam of ca. 100 μm in diameter at 45° to the normal of the sample surface. The apparatus was equipped with a 16 mm Balzers quadrupole mass spectrometer and Physical Electronics argon ion gun.

3. Results and discussion

In this section, the influence of positively charged Ar^+ ion beam on the sputtering process of the nonconductive boron nitride films will be discussed. The charge build-up effect for positive secondary ion sputtering is shown in Fig. 1. The distributions of positive $^{11}B^+$, $^{16}O^+$, $^{28}Si^+$ secondary ions show that after eroding 180 nm of the whole BN film, the sample charging disappeared. This indicates that the BN films with thicknesses lower than about 20 nm are not affected by charge build-up effects during both positive and negative SIMS characterization. Moreover, the sample charging effect is not so strong and does not move the energy distribution totally out of the energy window of the mass analyzer with the result that some positive secondary ions are detected. The ion intensities increase with the sputter time (depth) meaning that the sample charge disappears in thinner insulating films. In order to eliminate such effects during depth profiling, one can either apply neutralization of accumulating charge by electron bombardment [10] or perform negative secondary ion analysis [11]. For the negative ion detection such an effect does not work since negative ions can migrate through a positive electric field.

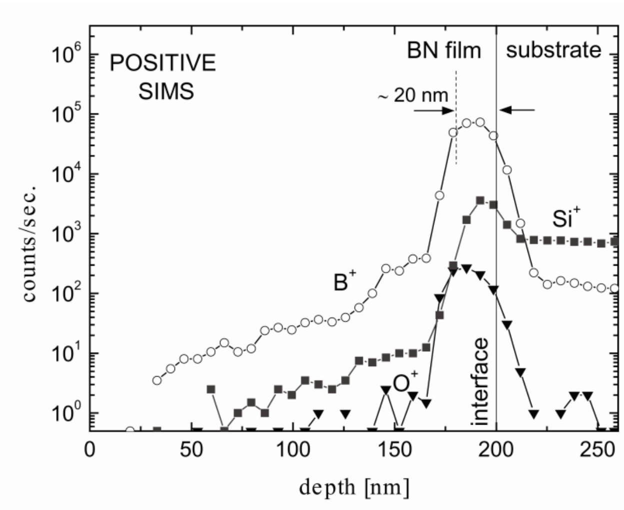

Fig. 1. Surface charging of the BN film during positive analysis of secondary ions: $^{11}B^+$, $^{16}O^+$ and $^{28}Si^+$

We focus on the investigation of BN films with the use of negative SIMS detection. We compare the depth profiles of two BN films (180 and 200 nm thick) deposited on a Si substrate at various flows of the gas source $(C_2H_5)_3B$ (2 cm^3/min – sample #1 and 3 cm^3/min – sample #2) to test nitrogen and boron incorporation into the film. This is shown in Fig. 2, where selected negative secondary ion signals are plotted in function of depth. The results show that the BN films and the BN/Si interface regions are highly oxidized, but in the case of sample #1, the effect is clearly visible which might worsen dielectric properties of a MIS device based on such a BN film. The thickness of the oxide layer at the substrate (BN/Si interface) is about 30 nm. Thus, surface charging for positive secondary ion analysis (Fig. 1) after partial recovery of the BN film might be less effective due to the much lower resistivity of the material closer to the BN/Si interface. However the presence of oxygen in the sputtering film increases the secondary ion yields, especially metals. In Figure 2, the secondary B^- intensity depends strongly on the oxygen distribution in the BN film that results in identical shapes of B and O profiles due to the so called matrix effects. Nitrogen is located in the interface region in the case of sample #1 and is rather more homogeneously distributed in the BN film of sample #2. Electrical measurements of complete MIS structures have shown better properties (higher resistivities) of the device based on the BN insulator fabricated at the gas flow of 3 cm^3/min (sample #2).

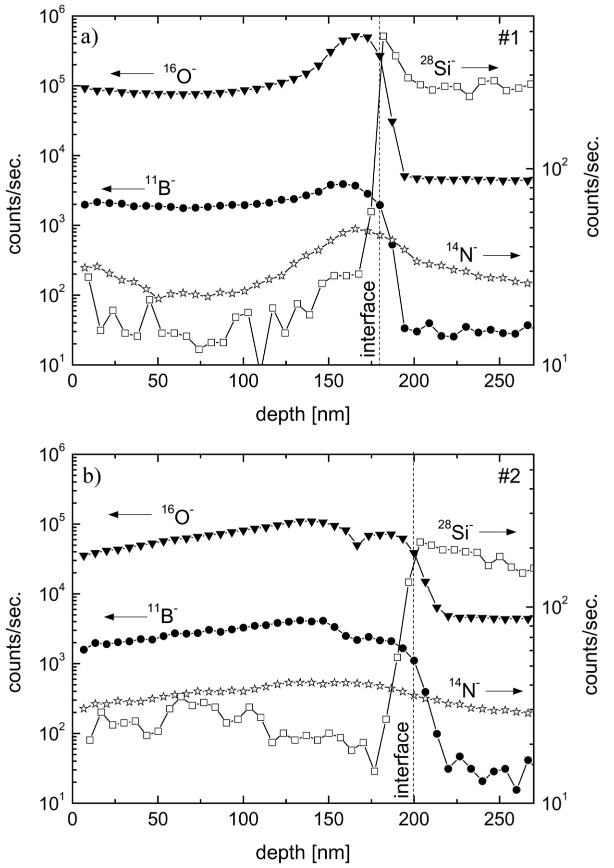

Fig. 2. Negative SIMS depth profiles of the boron nitride films deposited on Si-substrate using various source gas flows: a) 2 cm^3/min, b) 3 cm^3/min

In view of the fact that $^{28}Si^{2-}$ ion has the same mass to charge ratio as $^{14}N^-$ ion (also single-ionized molecule with two ^{14}N atoms has the same mass to charge ratio as $^{28}Si^-$; the ratio is 28 in both cases), the distribution of nitrogen can be overestimated, when silicon diffusion into the BN film is not excluded during BN film deposition. Selected mass interferences in SIMS analysis of the Al/BN/Si structures are shown in Table 1.

Table 1. Selected mass interferences in SIMS analysis of the Al/BN/Si structures

Ion mass [a.m.u.]	Ion
14	^{14}N, $^{28}Si^{2+/-}$, CH_2
28	$^{14}N_2$, ^{28}Si, C_2H_4
29	^{29}Si, $^{10}B^{19}F$
30	^{30}Si, $^{11}B^{19}F$
25	$^{11}B^{14}N$, C_2H
26	CN, ^{10}BO
38	$^{11}B_2O$, $Al^{11}B$
36	C_3, $^{11}B_2N$
43	AlO, $^{11}BO_2$

In order to completely eliminate multiple charged Si ion mass interference on nitrogen monitoring (especially in the interface region), the depth profiles of BN films deposited simultaneously on Si or on GaAs substrates have been determined.

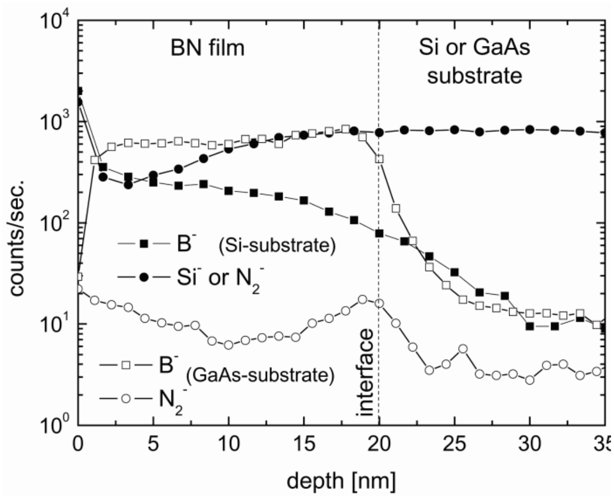

Fig. 3. Negative SIMS depth profiling of the BN films deposited on Si (full symbols) and GaAs (open symbols) substrates

Figure 3 gives an example of depth profiles for a thin 20 nm thick BN film on Si substrate compared with the depth profile of a thin BN film (the same thickness) deposited on GaAs substrate. We present negative SIMS analysis of $^{11}B^-$ and secondary ion intensities with mass equal 28 a.m.u. ($^{14}N_2^-$ and $^{28}Si^-$). The results show a remarkable difference in the ion signal measured for 28 a.m.u. species in films deposited at different substrates. These observations might indicate that Si diffuses into the BN film and leads to nitrogen signal overestimation in the BN/Si structure. We assume the same elemental concentration in both films, however there are some differences in boron profiles and no differences in oxygen intensities (not shown in the figure). However, oxygen presence in the BN film can highly increase the emission of silicon (diffused from substrate) during SIMS sputtering.

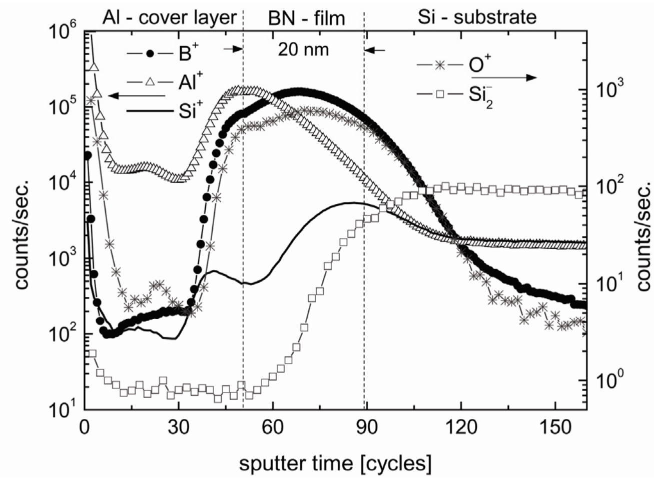

Fig. 4. Depth profiling of the Al/BN/Si MIS device
based on a 20 nm thick insulating BN film

The depth profile taken for negative and positive SIMS of complete MIS devices based on thin BN film is shown in Fig. 4. We select the 20 nm thickness of the gate insulator to avoid charge accumulation during positive ion measurements, which are desirable for Al layer characterization. In addition, the positive SIMS analysis allows one to exclude numerous mass interferences observed for the negative analysis. The interface regions are highly oxidized (Fig. 4) resulting in the increase of $^{27}Al^+$ (at the Al/BN interface) and $^{28}Si^+$ (at the BN/Si interface) emissions. Moreover, aluminum and silicon diffuse into the insulator. Thus higher content of oxygen located at the interfaces enhanced secondary ion yields of Al and Si measured in these regions. The profile of negative Si_2^- illustrates that such molecular ions are relatively matrix insensitive and represents more realistic concentration of silicon in the Al/BN/Si structures.

4. Conclusions

We have discussed Ar^+ SIMS depth profiling of thin boron nitride insulating films created on Si substrates. Charge build-up effects of the sample surface have been observed for positive ion detection when thickness of the insulating film is higher than about 20 nm. Negative mode of SIMS is proposed for depth profiling of such materials without compensating beam treatment. The elemental depth profiling in the BN films shows that basic constituent monitoring is affected by matrix effects caused by oxygen contamination (boron recording) as well as by ion mass interferences due to silicon diffusing from substrate (nitrogen recording). In order to find which of the features of the 14 a.m.u. species profile might be attributed to nitrogen, and which are due to Si diffusing from the substrate, the depth profiling should be derived from BN films deposited simultaneously on both Si and GaAs substrates. The study of complete MIS devices with Al electrodes in front of the BN insulators indicates also aluminum diffusion into the insulator.

Elemental depth profiling of BN films taking into consideration distribution of contaminations in the insulator or/and in the interface regions is a necessary step for achieving further progress in the MIS technology.

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