

Research on the piezoelectric response of cubic and hexagonal boron nitride films*

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Boron nitride (BN) films for high-frequency surface acoustic wave (SAW) devices are deposited on Ti/Al/Si(111) wafers by radio frequency (RF) magnetron sputtering. The structure of BN films is investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) spectra, and the surface morphology and piezoelectric properties of BN films are characterized by atomic force microscopy (AFM). The results show that when the flow ratio of nitrogen and argon is 2:18, the cubic BN (c-BN) film is deposited with high purity and c-axis orientation, and when the flow ratio of nitrogen and argon is 4:20, the hexagonal BN (h-BN) film is deposited with high c-axis orientation. Both particles are uniform and compact, and the roughnesses are 1.5 nm and 2.29 nm, respectively. The h-BN films have better piezoelectric response and distribution than the c-BN films.

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Boron nitride (BN) has five structures: cubic boron nitride (c-BN), hexagonal boron nitride (h-BN), rhombohedral BN (r-BN), wurtzite boron nitride (w-BN) and orthorhombic boron nitride (o-BN/e-BN). Due to the piezoelectric effect, h-BN has been used in the study of surface acoustic wave (SAW) devices^[1], but there is still no relevant report of preparation about the c-BN with more advantages, and the only applications in optics and electronics have been widely concerned^[2-4]. More importantly, c-BN with sp^3 bonding and sphalerite structure (zinc-blende) is the piezoelectric material^[5,6]. In addition, c-BN also has the similar SAW phase velocity (8000–10000 m/s) to the diamond, so the SAW phase velocity of the SAW devices with c-BN and diamond multilayer structure^[7,8] should be better than that of the ZnO/diamond^[9-11], AlN/diamond^[12-14] and h-BN/diamond SAW devices. Thus, when the interdigital transducer finger widths of SAW devices are the same, SAW devices of c-BN/diamond with multilayer structure can achieve higher frequencies. Both diamond and c-BN have very high thermal conductivity and low thermal expansion coefficient, so the high-frequency SAW devices with low-frequency dispersion and good frequency-temperature coefficient can be achieved. Therefore, it's important to

research the c-BN piezoelectric films.

In this paper, the BN films are prepared by radio frequency (RF) magnetron sputtering system, and it is found in the study that BN films with different structures can be prepared by changing the flow ratio of nitrogen and argon with the other conditions fixed. The deposited samples are tested by Fourier transform infrared (FTIR) spectrometer and X-ray diffraction (XRD) for structural characterization, and atomic force microscopy (AFM) for surface morphology and piezoelectric response.

Ti/Al bottom electrodes are prepared on Si (111) substrates by direct current (DC) magnetron sputtering. Al film is the bottom electrode, and Ti buffer layer is used to promote the nucleation of BN films and to improve the adhesion between BN films and Al electrodes. Then BN films are deposited on Ti/Al/Si(111) by RF magnetron sputtering device. The sputtering target is pure h-BN (99.95%) with the diameter of 60 mm. The distance from the target to the substrate is 65 mm. After the sputtering chamber is evacuated below 3.3×10^{-4} Pa and the substrate is heated to 500 K, high-purity nitrogen and argon (99.999%) gases are introduced into the chamber. The total sputtering pressure is kept at 0.8

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Pa, and the substrate negative bias is kept at -200 V. BN films are deposited at the RF power of 300 W for 120 min after presputtering for 30 min. In this study, the nitrogen to argon gas flow ratio takes 0:20, 2:18, 4:20 and 9:16, respectively.

In this study, the ingredients of the BN films are characterized by JASCO 4200 FTIR spectrometer. And the crystallinity and preferred orientation of the films are studied by Japan's Neo D-MAX2600 (18 kW) XRD. Surface morphology and piezoelectric properties of BN films are tested by AFM using the contact mode of piezoelectric response force microscopy (PFM).

Vibrational modes of BN films are infrared active, and the BN films are characterized by FTIR. Normally, h-BN has absorption peaks at 780 cm⁻¹ and 1384 cm⁻¹, and the c-BN has an absorption peak at 1065 cm⁻¹ [15]. Fourier transform infrared spectra of BN films deposited under different flow ratios of nitrogen and argon are shown in Fig.1. As the h-BN and c-BN have similar infrared sensitivity factor, ignoring the impact of the width of the absorption peaks, the cubic phase and hexagonal phase contents of the films could be estimated by

$$C^i = I_i / (I_{1065 \text{ cm}^{-1}} + I_{1380 \text{ cm}^{-1}}) \quad (1)$$

where $I_{1065 \text{ cm}^{-1}}$ and $I_{1380 \text{ cm}^{-1}}$ are the near-infrared absorption peak intensities at 1065 cm⁻¹ and 1380 cm⁻¹, respectively [16].

According to Fig.1, the relative contents of c-BN and h-BN are calculated by the absorption peak intensity under different flow ratios of nitrogen and argon, and the results are shown in Tab.1. It is shown that when only the argon gas, there is a clear h-BN absorption peak at 1365 cm⁻¹, and the content is 100%; when with a small amount of nitrogen and the flow ratio of nitrogen and argon is 2:18, the c-BN absorption peak intensity is at 1059 cm⁻¹, and the content of c-BN is 80.2%; when the flow ratio of nitrogen and argon is 4:20, the h-BN content is 100%; when the flow ratio is 9:16, the absorption peak is messy and there is an h-BN absorption peak at 1365 cm⁻¹. Thus, excessive or no nitrogen is not conducive to c-BN nucleation. When the barrier is nitrogen, it is not conducive to c-BN nucleation because h-BN target is bombarded by argon, with ionization into B ions and N ions, and free N ions react with N ions to nitrogen, making the number of N ions involved in film is reduced. The probability of compounding nitrogen atoms and boron atoms increases with the flow ratio of nitrogen and argon increasing, and the probability of BN films formation becomes larger. However, other forms of BN are formed when there are excess nitrogen and boron with the flow ratio of nitrogen and argon continually increasing and the c-BN formation inhibited.

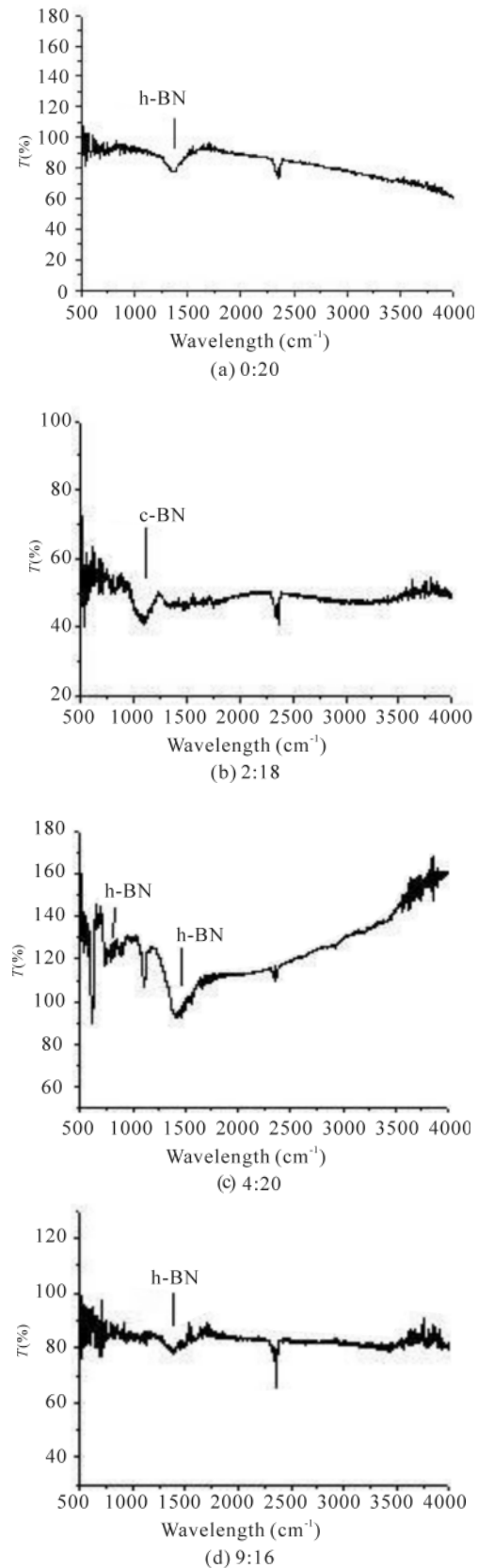


Fig.1 Fourier transform infrared spectra of the BN films deposited under different flow ratios of nitrogen and argon

Tab.1 Relative contents of c-BN and h-BN under different flow ratios of nitrogen and argon

Nitrogen partial pressure	0:20	2:18	4:20	9:16
c-BN(%)	0	80.2	0	/
h-BN(%)	100	19.8	100	/

As SiO₂ has absorption peaks in the range from 1100 cm⁻¹ to 1050 cm⁻¹, in this study, it is easy to believe mistakenly that the absorption peak of SiO₂ is c-BN. Therefore, the samples, deposited when the flow ratio is 2:18, are characterized by XRD, as shown in Fig.2. It can be seen that there are an h-BN (002) diffraction peak at 2θ = 26.52° and a c-BN (111) diffraction peak at 2θ = 42.8°, and both are with c-axis preferred orientation.

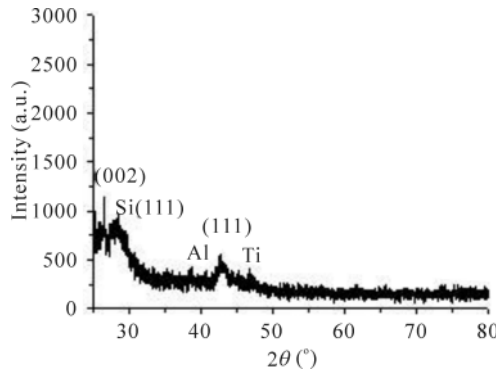


Fig.2 XRD pattern of BN films deposited when the flow ratio of nitrogen and argon is 2:18

In summary, higher levels of c-BN films are deposited by RF magnetron sputtering system when the flow ratio of nitrogen and argon is 2:18 with the other conditions fixed. Fourier transform infrared spectra of the samples show that there are absorption peaks at 1050 cm⁻¹ and 1340 cm⁻¹, and the relative intensity of absorption peaks is large. XRD shows that the c-BN is with c-axis preferred orientation. And h-BN films are deposited when the flow ratio is 4:20. The Fourier transform infrared spectra show that there are absorption peaks at 770 cm⁻¹ and 1372 cm⁻¹, and the absorption peak intensity at 1372 cm⁻¹ is significantly higher than that at 770 cm⁻¹, indicating the h-BN is with c-axis preferred orientation^[1].

AFM is used to study piezoelectric semiconductor materials, not only on its surface morphology characterization, but also for its piezoelectric properties characterization. Surface morphology images of BN films deposited under different flow ratios of nitrogen and argon are shown in Fig. 3. Fig.3(a) shows smaller particles with uniform size. Fig.3 (b) shows uniform particle size about 20-50 nm, and the root-mean-square (RMS) roughness of 3 im×3 im is 1.5 nm. Compared with Fig.3(b), Fig.3(c) shows more uniform particle size about 40-80 nm, and the RMS roughness is 2.29 nm. Fig.3(d) shows that the particle surface is uneven.

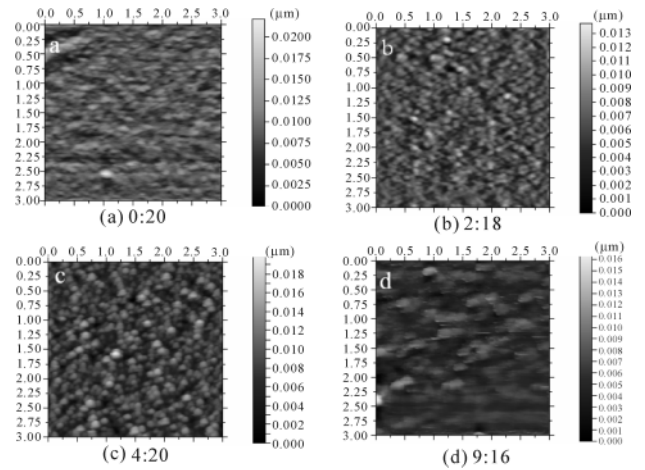


Fig.3 AFM images of the BN films deposited under different flow ratios of nitrogen and argon

The PFM images of BN films are shown in Fig.4. It can be seen that BN films have piezoelectric response. The BN films shown in Fig.4(b) and (c) have larger piezoelectric response, while more uniform distribution of piezoelectric response than that shown in Fig.4(a) and (d). Fig.4(c) shows the most uniform distribution of the piezoelectric response.

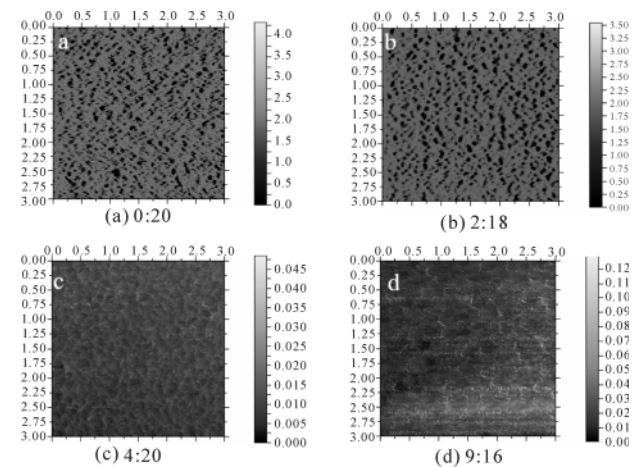


Fig.4 PFM images of the BN films deposited under different flow ratios of nitrogen and argon

In conclusion, in this study, the deposited c-BN films and h-BN films with uniform particle size and small surface roughness have piezoelectricity, and both meet the substrate material requirements of high-speed piezoelectric thin film nanostructure for GHz high-frequency SAW devices. However, h-BN has a stronger piezoelectric response and more even distribution of the piezoelectric response than c-BN, but the acoustic wave phase velocity of h-BN is smaller than that of c-BN.

In this paper, BN films are prepared by RF magnetron sputtering system through changing the flow ratio of nitrogen and argon on Ti/Al/Si (111), and characterized by FTIR,

XRD and AFM. The results show that when the flow ratio of nitrogen and argon is 2:18, the deposited c-BN films are highly c-axis oriented; when that is 4:20, the deposited h-BN films are c-axis oriented. Both of them are uniform and dense particles with piezoelectricity, and the roughnesses are 1.5 nm and 2.29 nm, respectively. h-BN has stronger piezoelectric response and more even distribution of the piezoelectric response than c-BN.

It is also shown that the substrate only with h-BN film and the multilayer structure composed of diamond substrates can be used for high frequency SAW devices. The multilayer structure composed of the c-BN films with higher speed of sound and diamond substrate can achieve ultra-high frequency SAW devices with low-frequency dispersion and good frequency-temperature coefficient. And these have great significance for the future design and development of high-frequency SAW devices.

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