Deposition of hexagonal boron nitride thin films on silver nanoparticle substrates and surface enhanced infrared absorption*

Deng Jin-Xiang(邓金祥)†, Chen Liang(陈 亮), Man Chao(满 超), Kong Le(孔 乐), Cui Min(崔 敏), and Gao Xue-Fei(高学飞)

School of Applied Mathematics and Physics, Beijing University of Technology, Beijing 100124, *China*

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Silver nanoparticle thin films with different average particle diameters are grown on silicon substrates. Boron nitride thin films are then deposited on the silver nanoparticle interlayers by radio frequency (RF) magnetron sputtering. The boron nitride thin films are characterized by Fourier transform infrared spectra. The average particle diameters of silver nanoparticle thin films are 126.6, 78.4, and 178.8 nm. The results show that the sizes of the silver nanoparticles have effects on the intensities of infrared spectra of boron nitride thin films. An enhanced infrared absorption is detected for boron nitride thin film grown on silver nanoparticle thin film. This result is helpful to study the growth mechanism of boron nitride thin film.

Keywords: hexagonal boron nitride thin film, silver nanoparticles, surface enhanced infrared absorption

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1. Introduction

There are four common poly types in the boron nitride system, which are: hexagonal (h-BN), rhombohedral (r-BN), cubic zincblende (c-BN), and wurtzite (w-BN). In the system, hexagonal boron nitride (h-BN) is the most stable equilibrium state with a graphite-like structure in which flat hexagonal sheets with sp^2 bonds are layered by an ABAB stacking sequence. In the past decade, various types of compounds containing π electrons (i.e., fullerenes,[1] nanotubes,[2] and one sheet of graphite) have attracted extensive interest in basic research because of their fascinating physical and mechanical properties due to their peculiar atomic structures. In addition, h-BN is one of the most interesting compounds with π electrons.[3] In its mechanical properties, h-BN is similar to graphite. It is also a typical layered material with strongly anisotropic chemical bonds, so h-BN is employed as a wear-resistant lubricant.[4] Interestingly, the electronic and optical properties of h-BN are clearly different from those of graphite. Hexagonal boron nitride is a wide-gap semiconductor with high electrical resistivities, low dielectric losses, and good transmittances in a wide spectral range, from visible to infrared and up to the microwave. It also shows excellent thermal conductivity and stability, low density, and high chemical inertness. By virtue of the above outstanding properties, h-BN is widely used in vacuum technology, microelectronic devices,[5] and optical devices,[6] especially in some special applications at high temperatures.

High purity h-BN powder can be grown under high pressure and high temperature (HP/HT). In fact, h-BN thin film has more significance in h-BN optical and electronic industry applications. The h-BN thin films can be grown on various substrates, such as Si,[7] SiC,[8] Al_2O_3,[9] Ni,[10] steel,[11] etc. In this paper, h-BN thin film is deposited on a substrate of silver nanoparticle thin film. It was reported that silver nanoparticles can enhance optical absorption in a thin film Si solar cell.[12] Here, an enhanced infrared absorption with silver nanoparticles is detected for the h-BN film, which is helpful to study the growth mechanism of boron nitride thin films and to use them in optoelectronics. This is the first study to realize an enhanced infrared absorption of boron nitride thin film using silver nanoparticles.

2. Experiment

The p-type Si (100) ($\rho = 10\ \Omega\cdot$cm$\sim$20 $\Omega\cdot$cm) wafer was cut into 1 cm$^2\sim$2 cm^2. These Si substrates were ultrasonically cleaned in methylbenzene, acetone, deionized water, and methanol for 15 min in sequence, and then stored in methanol in a dark and cool place. Prior to deposition, these Si substrates were dried in a dry nitrogen flow. Silver nanoparticles substrates (silver nanoparticle interlayer) were fabricated through depositing silver nanoparticles on these silicon substrates by a radio frequency (RF) magnetron sputtering system of 13.56 MHz. Then, boron nitride films were deposited on the silver naoparticle substrates by the radio frequency magnetron sputtering system. We used silver and hot-pressed hexagonal boron nitride (h-BN) as targets. In the experiment, the

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†Corresponding author. E-mail: jdeng@bjut.edu.cn

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sputtering targets were 100-mm diameter disks laid on the underside of the cathode, which was linked with a RF generator (13.56 MHz) through a matching network. The substrate holder was located on the anode, on which there were heating and biasing apparatuses for substrates. A magnetic coil was employed to produce a magnetic field that could restrict the movement of electric particles in the plasma in order to increase the density of plasma between target and substrate. The distance between the target and the substrate was set to be 6 cm.

The vacuum chamber of the radio frequency magnetron sputtering system was evacuated to a background pressure of lower than 1×10^{-3} Pa. The deposition was carried out in an Ar gas for silver nanoparticles and a gas mixture of Ar/N_2 for boron nitride films, separately. During deposition of boron nitride thin films reactive nitrogen was supplied to the discharge to produce the stoichiometric boron nitride films. These two kinds of gases were supplied into the deposition chamber, each using an MKS multi-gas controller. The used gases had a purity of 99.999%. The silver nanoparticles and boron nitride layers were sequentially deposited on the p-type Si (100) substrates by using radio frequency magnetron sputtering. The deposition conditions for silver nanoparticle interlayer and BN films are summarized in Table 1.

Table 1. Deposition conditions for silver nanoparticles interlayer and BN film.

	Step 1	Step 2
Targets	99.99% silver	99.99% h-BN
Substrates	P-type Si (100)	silver nanoparticles interlayer
Working gas	Ar	$Ar+N_2$, $Ar:N_2$=6:4
Working pressure/Pa	1	1
RF power/W	40, 60, 80	150
Substrate temperature	room temperature	room temperature
Time	5 s	20 min, 40 min
Negative bias/V	0	0

The Fourier transformed infrared spectroscopy (FTIR) (WQF–310, 400 cm^{-1}~4000 cm^{-1}, scanning step 4 cm^{-1}) was employed to characterize the boron nitride thin films. The background spectrum of the uncoated substrate was deducted. In addition, the surface morphologies and the grain sizes of films were obtained using an atomic force microscope (AFM) (FEI Quanta 600F).

3. Results and discussion

Figure 1 shows the AFM images of silver nanoparticle interlayer surfaces on Si, which are formed under different sputtering powers with the same sputtering time of 5 s. From Fig. 1 the average grain sizes are obtained to be 126.6±6.6, 78.4±7.3, and 178.8±6.0 nm for sputtering power of 40, 60, 80 W, respectively, and the root-mean-square (RMS) roughness values of silver nanoparticle interlayer surfaces are also obtained and depicted in Fig. 2. It is obvious that sputtering power has an effect on the morphology of silver nanoparticle interlayer surface. The formation of the film is likely to experience the following process. Within the sputtering time of 5 s, and at a definite substrate temperature when the sputtering power is 40 W, fewer silver atoms or particles reach the surface of Si. The nucleation centers are less, so silver atoms or particles can move a longer distance to combine with nucleation centers to form big islands. As the sputtering power increases to 60 W, more silver atoms or particles reach the surface of Si, so that the islands grow bigger rapidly and are agglomerated to form larger silver islands.[13] Furthermore, the islands are linked together to form a continuous and smooth surface. Then, many small islands are formed again on the smooth surface. However, when the sputtering power increases to 80 W, the film growth process is similar to that when the sputtering power is 60 W and more silver atoms or particles reach the surface so that the small islands formed on the smooth surface have a chance to grow bigger. That may be why the average grain size in the film changes from big to small and then further to big as the sputtering power increases. From Fig. 2 it can be seen that RMS roughness value of silver nanoparticles reaches a minimum value at 60 W of sputtering power.

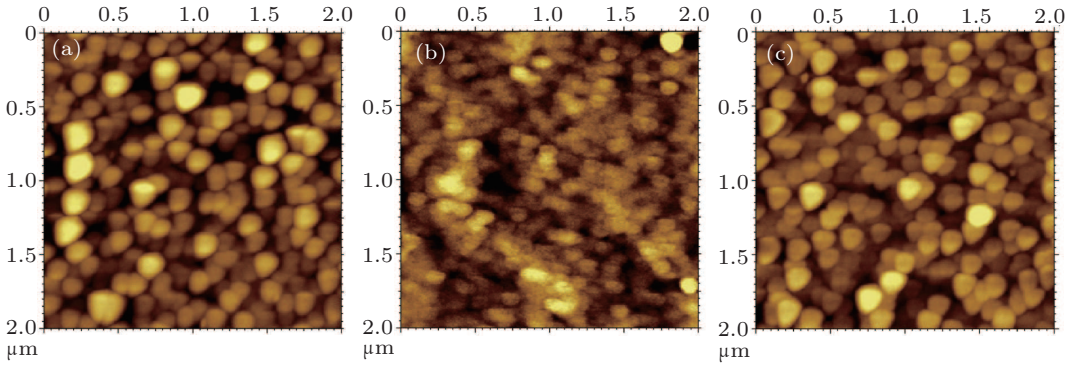


Fig. 1. (color online) AFM images of silver nanoparticle interlayer surfaces on Si formed respectively under sputtering powers of (a) 40 W, (b) 60 W, and (c) 80 W with the same sputter time 5 s.

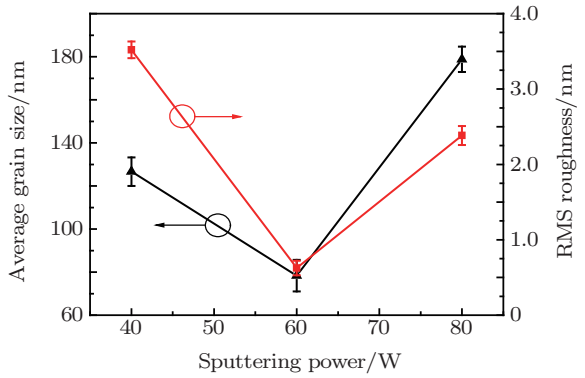


Fig. 2. (color online) Average grain size and RMS roughness value of silver nanoparticle interlayer surface versus sputtering power.

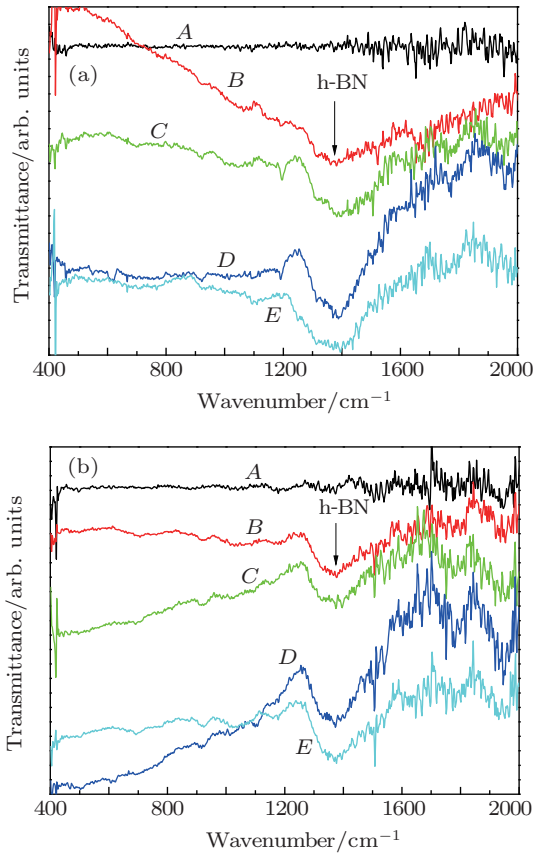


Fig. 3. (color online) FTIR spectra of BN thin films deposited on different substrates. The deposition times of BN are (a) 20 min and (b) 40 min. The substrates for depositing BN are (curve *B*) Si, and (curve *C*) Si/40 W, (curve *D*) Si/60 W, (curve *E*) Si/80 W sputtered silver nanoparticle interlayer. Curve *A* represents the FTIR spectrum of silicon substrate without BN and Ag.

Figure 3 shows the FTIR spectra of BN thin films deposited on different substrates. The deposition times of BN are (a) 20 min and (b) 40 min. The substrates to deposit BN are (curve *B*) Si, and (curve *C*) Si/40 W, (curve *D*) Si/60 W, (curve *E*) Si/80 W sputtered silver nanoparticles interlayer. In Fig. 3, curve (*A*) is used for the FTIR spectrum of silicon substrate without BN and Ag. Absorption peaks near 1380 cm^{-1} are from h-BN in Fig. 3. In Fig. 3(a), the h-BN absorption peaks for the films deposited on different silver nanoparticle substrates each have a slight shift. The reason for this cannot be explained for the moment, so further investigation is needed. From Fig. 3, it can be seen that the intensity of h-BN thin film on silver nanoparticle interlayer is greater on Si(*B*) (see curves *C*, *D*, and *E*). In order to discuss the problem conveniently, relative intensity I is introduced as follows:

$$I = \frac{I_{\mathrm{Si+Ag}}}{I_{\mathrm{Si}}}, \tag{1}$$

where I_{Si} is the IR spectrum intensity of h-BN thin film deposited on silicon substrate without silver, and $I_{\mathrm{Si+Ag}}$ is the IR spectrum intensity of h-BN thin film deposited on silver nanoparticle interlayer grown on silicon. Based on spectrum data in Fig. 3 and formula (1), the results in Fig. 4 are obtained. From Fig. 4 it follows that $I > 1$ for all the data point, so that it can be concluded that silver nanoparticles formed on the surface can enhance the infrared absorption of h-BN thin films.

By combining Fig. 4 with Fig. 2 it can be seen that the average grain size of silver nanoparticles has an influence on surface-enhanced infrared absorption of h-BN thin film. Here, we denote the average grain size of silver nanoparticles as symbol d. In Fig. 2 for sputtering powers of 40 W, 60 W, 80 W, the values of d are 126.6 nm, 78.4 nm, and 178.8 nm, respectively. Furthermore, by combining Fig. 4 with Fig. 2, for h-BN thin films on different silver interlayers relative intensity I first increases then decreases with d increasing. When $d = 78.4$ nm, the relative intensity I reaches its maximum.

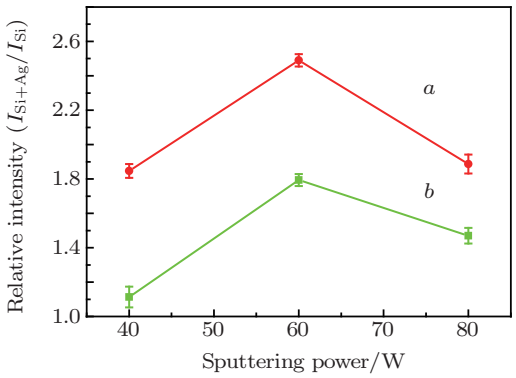


Fig. 4. (color online) Relative intensities of BN thin films deposited on different silver nanoparticle interlayers versus sputtering power. The deposition times of BN are (a) 20 min and (b) 40 min.

As is well known, silver island film exhibits a distinct absorption band in the visible region due to the transverse collective resonance of free electrons in metal. This resonance is caused by incident radiation polarized in the direction parallel to the array of metal islands if the island size is much smaller than the radiation wavelength. This resonance can generate an enhanced electromagnetic field near the metal surface, thereby contributing to the enhancement of visible absorption by the surface molecules.[14] It is also recognized that the absorption band due to the resonance shifts towards a longer wavelength and becomes broad with the increase of film thickness

because of the increased lateral dipole–dipole interaction of the metal islands. Thus, it follows that closely packed metal islands are favorable for collective electron resonance in the infrared region.[14] These are the reasons why the aggregation state of the metal islands can enhance the infrared absorption of molecules in a thin film deposited on the metal islands. According to Ref. [15] only those vibrations that are accompanied with a change in dipole moment perpendicular to the microscopic surfaces are enhanced. In Fig. 3, the peak near 1380 cm^{-1} represents a stretching of the B–N bond within the basal plane of h-BN,[16] which results in a change in dipole moment along the B–N bond. During the deposition of h-BN thin films, we purposely applied no heating or biasing to the substrates. Under such conditions, the basal plane of h-BN is randomly oriented.[16] Therefore, in the h-BN films there are changed components of dipole moment referring to the B–N bond, which are perpendicular to the surfaces of silver islands. So, in our experiments silver nanoparticle interlayers can realize surface-enhanced infrared absorption of h-BN thin film.

However, we need to ask why the value of d and thickness of h-BN thin film affected the value of relative intensity I in our experiment? It is generally accepted that the enhancement does not occur on the entire surface of the metal islands and takes place only at the edges of the metal islands.[15] For our sample, when sputtering power is 60 W and the smallest value of d is 78.4 nm (i.e., $d = 78.4$ nm) the number of silver islands is maximised. So, the edges of the silver islands are maximised, which results in maximum relative intensity I compared with those of the same thick h-BN thin films. There is also evidence that the enhancement is restricted within narrow regions that are in contact with the metal islands. For silver islands the enhancement is saturated at a distance of 3 nm–5 nm from the silver surface.[17] In our experiment the thickness values of h-BN thin films are between 60 nm and 120 nm, which are much larger than 3 nm–5 nm. When the h-BN thin film is thick enough, only a very thin layer (3 nm–5 nm thick) is in contact with silver islands, which could enhance the infrared absorption. The thicker the h-BN thin film, the smaller the relative intensity I is. Because the enhancement is the same, the intensity of h-BN thin film absorption increases as the thickness of h-BN thin film increases. This is why in Fig. 4 the value of I (I_{Si+Ag}/I_{Si}) in curve a is larger than that of I in curve b.

This gives a view of the formation of a cubic boron nitride thin film; that is, the cubic phase is transformed from a hexagonal phase. This process is generally detected by IR spectrum. The surface enhanced infrared absorption of silver islands could be used to investigate the process and is more conducive to their applications in optoelectronics.

4. Conclusion

Silver nanoparticle thin films with different average particle diameters are grown on silicon substrates, and boron nitride thin films are deposited on the silver nanoparticle interlayer by radio frequency magnetron sputtering. The average particle diameters of silver nanoparticle thin films are 126.6, 78.4, and 178.8 nm. The results show that the sizes of the silver nanoparticle can affect the intensities of infrared spectra of boron nitride thin films. An enhanced infrared absorption is detected for the boron nitride thin film grown on silver nanoparticle thin film. This result is helpful to study the growth mechanism of boron nitride thin film.

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