Theoretical study on critical thickness of heteroepitaxial h-BN on hexagonal crystals

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Jiadong Yu, Lai Wang *, Zhibiao Hao, Yi Luo *, Changzheng Sun, Yanjun Han, Bing Xiong, Jian Wang, Hongtao Li

Tsinghua National Laboratory for Information Science and Technology, Department of Electronic Engineering, Tsinghua University, Beijing 100084, People's Republic of China

A B S T R A C T

Hexagonal crystals are suitable underlayer candidates for hexagonal boron nitride (h-BN) heteroepitaxy due to their similar in-plane atomic arrangement. When the thickness of h-BN is beyond a critical value, its accumulated stress resulting from the lattice mismatch can be relaxed by generating dislocation or changing into three-dimensional growth. Here we calculate the evolution of h-BN critical thickness with the growth temperature when it is grown on various frequently-used hexagonal crystals for both cases. The results show that in order to minimize the lattice mismatch, a low growth temperature is preferred when grown on GaN or Si(1 1 1) while on the contrary when grown on 6H-SiC or α-Al$_2$O$_3$. Besides, AlN is the most unique underlayer as its lattice mismatch with h-BN is relatively small (<0.7%) and they can even fully match around 1150 K, which means it can be used as a buffer layer for thick h-BN (>100 nm) growth. Moreover, large area of two-dimensional thin h-BN (5–15 nm) layer can be obtained on GaN, 6H-SiC, Si(1 1 1) or α-Al$_2$O$_3$ except for graphene. On the other hand, calculation indicates that large area of graphene can be grown on h-BN.

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1. Introduction

Hexagonal boron nitride (h-BN), which has a graphene-like sp^2-bonded two-dimensional (2D) layered structure, is a promising material for release layer of GaN-based devices' mechanical transfer [1,2] as well as fabricating deep ultraviolet optical device [3], which can be attributed to its wide band gap approximately around 5.9 eV [4] and relatively low acceptor ionization energy [3]. Besides, large-scale h-BN film has received a great deal of attention as a substrate for high-performance graphene nanodevices [5–7]. Due to the same in-plane atomic arrangement, it is better to use hexagonal crystals as the underlayers for h-BN heteroepitaxy, such as AlN [3,8], GaN [9], α-Al$_2$O$_3$ [10–12], Si (1 1 1) [13] and 6H-SiC [14]. However, because of the lattice mismatch with these foreign underlayers, h-BN will suffer from misfit stress during growth. When it exceeds a critical thickness (h_c), the accumulated stress will be relaxed in some possible ways [15]: one is dislocation generation, which will degrade the crystal quality, and the other is three-dimensional (3D) growth, which will roughen the surface. Thus, in order to obtain high quality and uni-

form h-BN film with large scale, it is necessary to study its critical thicknesses in both cases, but they were seldom reported in previous study. Besides, h-BN as a kind of 2D material has weak interaction between atomic layers, so the strain could also be relieved by rippling [16] or cracking [17], especially in the first few layers. These effects should be studied by *ab initio* calculation, which will not be discussed in the present paper.

In this paper, we only consider the effect of dislocation generation and 3D growth, and choose the calculation models mainly considering their consistency with the reported values. The critical thicknesses of h-BN on frequently-used hexagonal crystals are investigated theoretically taking the thermal expansion of lattice constant into account, and also compared with reported experimental results. The paper is organized as follows. Firstly, based on the existing theories on critical thickness for dislocation generation (h_{c-dis}) [18–21] and 3D growth (h_{c-3D}) [22,23], we select the most practical models to calculate h_{c-dis} and h_{c-3D}, through verifying their consistency with the published results of h-BN grown on graphene and Cu(1 1 1). Then, we use these models to calculate the evolution of h_{c-dis} and h_{c-3D} with growth temperature for h-BN grown on various hexagonal crystals as well as for graphene grown on h-BN. The calculation results are discussed combining with the published experimental data. Finally, we put forward some reasonable ways of growing h-BN for different applications.

2. Theoretical models

2.1. Critical thickness for dislocation generation (h_{c-dis})

There are two general models (from the force's and energy's view points respectively) to calculate the critical thickness for dislocation generation. Matthews et al. [18] thought that the strain originating from the lattice mismatch will exert a force (F_{elas}) on dislocation line. When F_{elas} is larger than the tension of dislocation line (F_{dis}), dislocation will be generated as a result of plastic flow at the interface. On the other hand, People et al. [19] believed that elastic energy will accumulate during film growth if there is lattice mismatch between epilayer and substrate. When elastic energy is higher than the strain energy of dislocation, dislocation will be generated to release the strain. Besides, other energy balance models have also been developed by Van der Merwe [24] and Matthews [25], which can predict the same critical layer thickness as the force balance model, as long as appropriate assumptions are made. These two types of models only consider the interaction between dislocation and film, but exclude the interaction between different dislocations. So the calculated critical thickness will be overestimated when the interaction between atomic layers is weak, especially in the case of 2D material such as h-BN. Holec et al. [26] also proposed a model based on a balance of energy which is more appropriate for describing the critical thickness of the wurtzite III–nitride materials system. This model need more calculation parameters which is difficult to obtain the reliable values for h-BN at present. Furthermore, Fischer et al. [20] proposed an easy-to-use method in equilibrium theory for strain relaxation which includes the elastic interaction between misfit dislocations. By considering the exact solution for elastic interaction of real and image dislocations, their equilibrium model can describe the strain relief via plastic flow. In brief, the critical thickness can be deduced from [20]

$$\varepsilon_{xx} \cos \phi = \frac{b}{2h_{c-dis}} \left(1 + \left(\frac{1 - v/4}{4\pi \cos^2 \lambda (1 + v)} \right) \ln \left(\frac{h_{c-dis}}{b} \right) \right) \quad (1)$$

where ε_{xx} is the lattice mismatch between fully relaxed epilayer and substrate, v is the Poisson's ratio, and b is the Burgers vector, ϕ is the angle between the slip plane and the strained interface normal, and λ is the angle between the Burgers vector and the direction in the interface (normal to the dislocation line).

As a kind of 2D-materials, the dislocation types of h-BN are a little different from those of other III-nitride materials with wurtzite structure. There are two types of Burgers vectors, $b = a$ (pentagon-heptagon pairs (5|7 s)) and $b = \sqrt{2}a$ (square-octagon pairs (4|8 s)) [27], both of which belong to a-type dislocations. And it can be found that $\phi = 0°$, and $\lambda = 0°$ in these a-type dislocations. According to the previous report [28], the h_{c-dis} for h-BN film on graphene is around 6.3 nm under different circumstances. Inserting appropriate material parameters, $\varepsilon_{xx} = 2\%$ [28], $b = 2.504$ nm [3], $v = 0.177$ [29], the calculated h_{c-dis} of h-BN is 7.6 nm, which is in good agreement with the experimental value. Then we use Fischer's model to calculate the h_{c-dis} of h-BN in next section.

2.2. Critical thickness for 3D growth (h_{c-3D})

The most widely-accepted method for calculating critical thickness of 3D growth is Nakajima's model [22]. It considers that if the sum of the surface free energy density of epilayer (E_{epi}^{surf}), the elastic strain energy density (E_{elas}) and the interfacial energy density (E_{int}) is more than the surface free energy density of substrate (E_{sub}^{surf}), there will be a three-dimensional growth to release the elastic strain energy, as shown in Eq. (2).

$$E_{epi}^{surf} + E_{elas} + E_{int} > E_{sub}^{surf} \quad (2)$$

The formula to calculate E_{int} is as follows:

$$E_{int} = E_{sub}^{surf} \left(1 - \frac{1}{\varepsilon_{xx} + 1} \right) \quad (3)$$

Finite element method is used to calculate E_{elas}, wherein the epilayer is divided into m imaginary thin layers and the total E_{elas} can be calculated as follows:

$$E_{elas} = \sum_{i=1}^{m} E_i = \sum_{i=1}^{m} \frac{d_i \sigma_i^2}{2Y_i} \quad (4)$$

where E_i, d_i, σ_i and Y_i are the energy density, thickness, stress and Young's modulus of the i th imaginary layer, respectively. In order to simplify the calculation process, an alternative approach [19] is proposed. Assuming the epilayer is an uniform thin layer, the elastic strain energy density associated with a film of thickness h is given by:

$$E_{elas} = 2G \frac{1-v}{1+v} \varepsilon_{xx}^2 h \quad (5)$$

where G is the shear modulus. Combing Eqs. (2), (3) and (5) along with E_{epi}^{surf} and E_{sub}^{surf}, the h_{c-3D} can be calculated. The previous study [30] has shown that h_{c-3D} for h-BN film on Cu(111) is around 1.8 nm. Inserting appropriate material parameters, $E_{h-BN}^{surf} = 12.9$ meV/Å² [31], $G = 46.8$ GPa [32], $v = 0.177$ [29], $\varepsilon_{xx} = 10.6\%$ [3,33], $E_{Cu(111)}^{surf} = 112.4$ meV/meV/Å² [33], the calculated h_{c-3D} of h-BN is 2.4 nm, which is very close to the experimental value. Thus we use this simplified model to calculate the h_{c-3D} of h-BN in next section.

3. Calculation results and discussion

The evolutions of h_{c-dis} and h_{c-3D} with growth temperature on frequently-used hexagonal crystals, such as AlN, GaN, 6H-SiC, Si (111), α-Al₂O₃ and graphene, are studied using the models mentioned above. The surface energies [15,34–38] of different under-layers are listed in Table 1. Besides, both Burgers vector b and lattice mismatch ε_{xx} depend on the lattice constant of h-BN and underlayers. Considering the thermal expansion effect of lattice, they will change along with growth temperature. The thermal expansion coefficients of h-BN, AlN, GaN, 6H-SiC, Si(111), α-Al₂O₃ and graphene can be found in Refs. [39–44] (see Figs. S1–S7 in Supplementary Materials). Then, temperature-dependent lattice constants can be obtained.

3.1. Heteroepitaxial h-BN on AlN, GaN and 6H-SiC

According to Ref. [3], every five h-BN atoms will align with four AlN atoms along the a-direction, so there exists a 5/4 coincidence at the h-BN/AlN hetero-interface. Consequently, the lattice mismatch is calculated as $(5a_{h-BN} - 4a_{AlN})/4a_{AlN}$. The evolutions of lattice mismatch, h_{c-dis} and h_{c-3D} of h-BN on AlN with growth temperature are shown in Fig. 1. Lattice mismatch between h-BN and AlN is relatively small (<0.7%), so it is conducive to growing thick h-BN (>100 nm) with large area on AlN. They will reach nearly lattice matching when growth temperature is around 1150 K, hence h_{c-dis} and h_{c-3D} can reach its maximum. However, given the surface migration of boron adatom, the typical growth temperature in experiments is about 1300–1500 °C [8,45]. It can also be seen from Fig. 1 that h_{c-dis} with difference b (a and $\sqrt{2}a$) is much less than h_{c-3D}, which means stress of h-BN heteroepitaxy on AlN will release through generating dislocations (edge type) preferentially. Thus, smooth h-BN film with large-scale can be