Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Investigation on cubic boron nitride crystals doped with Si by high temperature thermal diffusion

Xinlu Li[a], Shuang Feng[a], Xiuhuan Liu[b,*], Lixin Hou[c], Yanjun Gao[a], Qi Wang[a], Nian Liu[a], Hai Zhang[a], Zhanguo Chen[a,*], Jie Zheng[a], Gang Jia[a]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[b] College of Communication Engineering, Jilin University, 5372 Nanhu Road, Changchun 130012, China
[c] College of Information and Technology, Jilin Agricultural University, 2888 Xincheng Street, Changchun 130118, China

ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form 28 March 2014
Accepted 7 April 2014
Available online xxx

Keywords:
Cubic boron nitride
Si impurities
Thermal diffusion
XPS
Activation energy

ABSTRACT

The method of high temperature thermal diffusion was successfully applied for doping Si impurities into cubic boron nitride (cBN) crystals. X-ray photoelectron spectra (XPS) and the current–voltage (*I–V*) characteristics at different temperatures were respectively used for analyzing the chemical states and the activation energy of Si impurity in cBN. According to the XPS results, Si impurities mainly replace B atoms bonding with the adjacent N atoms and become donors in cBN. Without surface cleaning, there are a lot of C and O contaminations on the surface of cBN, so a small quantity of C–Si and Si–N–O bonds also exist at the surface of cBN. Most Si impurities distribute in the shallow layer underneath the surface of cBN. Based on the electric measurement, Si impurities in cBN usually have the activation energy beyond 0.4 eV, and they can only be slightly ionized at room temperature, therefore the resistivity of Si-doped cBN is still high, and the space charge limited current becomes the main conductive mechanism in cBN. However, the conductivity of Si-doped cBN can rapidly increase with the temperature. In addition, the activation energy and the concentration of Si impurity in cBN can be affected by the temperature and the time of thermal diffusion, which needs to be verified further.

1. Introduction

Cubic boron nitride (cBN) is a kind of synthetic material [1]. The hardness of cBN is second only to diamond, so the cBN crystal is widely used as an abrasive and a cutting tool [2]. As a wide bandgap semiconductor, cBN has many excellent physical and chemical properties and attracts people's great research interest in recent years [3–5]. The cBN crystal has a high thermal conductivity (~13 W/cm K) [6], a low dielectric constant (~7.1) [7], the largest bandgap (~6.4 eV) in III–V compounds and IV material [8], a high intrinsic breakdown electric field (~8 MV/cm) [9], very high thermal stability and chemical stability. Thus, cBN has important potential applications in high-temperature and high-power electronic devices, and UV optoelectronic devices [5,11,12]. Especially, compared with diamond and ZnO etc., cBN can be doped into both P-type and N-type materials, so that it is easily to fabricate the stable homogeneous p–n junction [10–12]. Under high pressure high temperature (HPHT), Mishima et al. succeeded in manufacturing a diode based on a cBN single crystal, which still had good rectification characteristics even at 530 °C [10]. Be, Mg, Zn, etc., are commonly used as P-type dopants in cBN [13–15], and the elements of group VI, such as S and O, tend to occupy the N lattice sites and become donor impurities in cBN [16,17]. As for group IV elements such as C and Si, etc., they are amphoteric impurities because they not only can occupy the B lattice sites and become donors [18], but also may replace N atoms as acceptors [19]. Thus, it is necessary to deeply analyze the chemical structures of group IV elements in cBN crystals [20].

At present, the common doping methods include in situ doping and ion implantation for cBN crystals [10–16]. As for the in suit doping, dopant atoms often inhibit the nucleation of cBN crystal, which results in impure phases and nonuniform distribution of impurities in cBN crystals [12,14]. Precisely and uniformly doping can be carried out by ion implantation. However, this method is very costly, and the sample surfaces are often damaged by the ion beam with high energy. Diffusion is another conventional doping technique, which is cheap, easy-handled and uniform. But very few reports on the diffusion doping of cBN crystals are found [21].

* Corresponding authors. Tel.: +86 431 85168382; fax: +86 431 85168270.
E-mail addresses: xhliu@jlu.edu.cn (X. Liu), czg@jlu.edu.cn (Z. Chen).

http://dx.doi.org/10.1016/j.apsusc.2014.04.059
0169-4332/

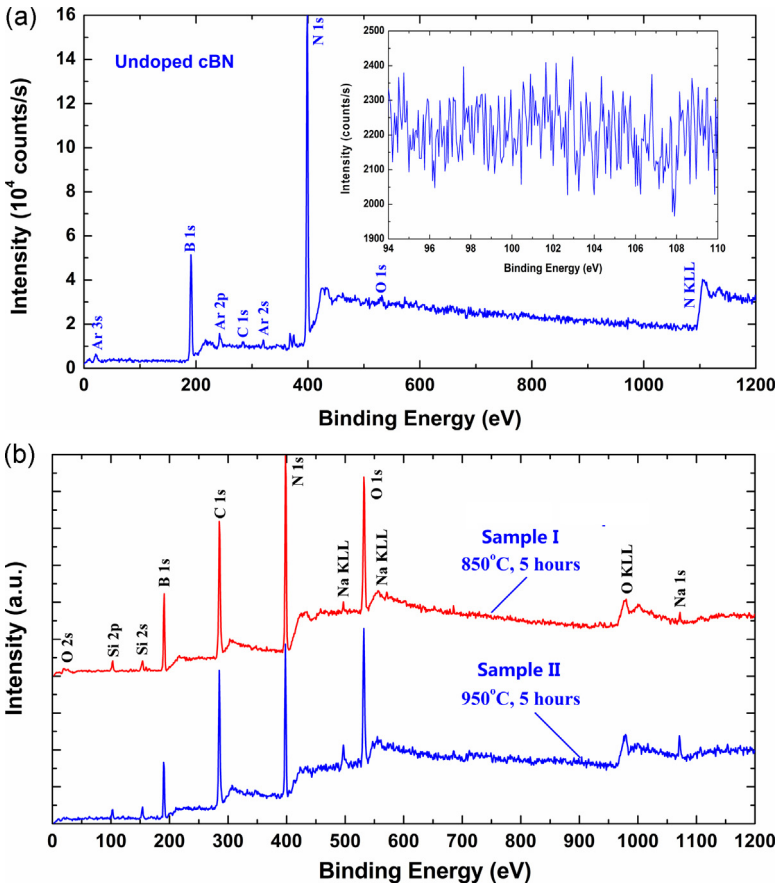

Fig. 1. The XPS spectra of cBN crystals. (a) The XPS spectra of cBN crystals sputtered by Ar ion beam before being doped. The insert is the narrow scan near the binding energy of Si 2p, and no peaks exist. (b) The XPS spectra of Si-doped cBN sample I and II without Ar ion sputtering. Obvious Si2p and Si2s peaks are observed.

In this paper, a diffusion method was adopted to dope cBN crystals with Si powders, and the chemical state of Si impurities in cBN was investigated by X-ray photoelectron spectroscopy (XPS). In addition, the effects of diffusion time and temperature on the concentration and the activation energy of Si impurities were discussed too.

2. Experiments

The plate-like cBN crystals were synthesized under HPHT condition. The transverse size of cBN is about 500 μm on average, and the thickness is about 100 μm. We have described them in details before [22]. The cBN samples were treated before thermal diffusion. Firstly, the cBN samples were soaked in aqua regia for 10 min and rinsed by deionized water. Then they were put into toluene, acetone and ethanol for ultrasonic washing for 10 min, respectively. Finally, the samples were rinsed with deionized water and dried with a drying oven.

The dopant is Si powder with the purity of 99.99% and the average size of 6.5 μm. First, a layer of Si powder was spread at the bottom of a clean quartz boat, and then the small cBN samples were sprinkled on the Si powder and buried with enough Si powder, then the powder was compacted and covered by a silicon wafer in the quartz boat. The quartz boat was pushed into the quartz tube of a horizontal vacuum tube furnace, and the mechanical vacuum pump was turned on. When the pressure of the tube is below 10 Pa, the tube was purged with high purity N_2 flow. According to the reported result, 850 °C seems to be more feasible for thermal diffusion [23], so the tube was heated up to 850–950 °C and kept the temperature for 4–5 h. After the heating, with the power source turned off, the quartz tube began to cool down to room temperature naturally. The mechanical pump was shut down at last. The Si-doped cBN samples were taken out from the furnace, and were soaked with a mixture solution of HNO_3 and HF (the volume ratio is 1:1) to remove the residual Si powder at the surfaces of the cBN samples. Then the samples were rinsed by the deionized water, and cleaned by toluene, acetone and ethanol for ultrasonic for 10 min, respectively. Finally, the cBN samples were dried after being rinsed again by the deionized water and kept for the next measurement.

In order to analyze the chemical components and structures of the cBN samples, the XPS spectra were measured by an ESCALab 250 spectrometer with a focused monochromatic Al Kα ($h\nu$ = 1486.6 eV) X-ray beam with a diameter of 200 μm. The background pressure in the analysis chamber at room temperature was in the range of 10^{-8} to 10^{-9} Pa. Initial survey scans were performed under the pass energy of 50 eV. As for narrow scans of some main elements, the pass energy is 20 eV. The binding energy scales of the samples were referenced to the C–C/C–H peak at 284.6 eV to eliminate the effect of surface charging. For removing the contamination of C and O, etc., the Ar ion beam (2 kV, 2 μA) was applied to sputter the surfaces of the cBN samples for 5 min. After sputtering, the Ar $2p_{3/2}$ line at 241.4 eV [24] was used for charge referencing. The XPS peaks were fitted by using a Gaussian-Lorentzian curve fitting program after Shirley background subtraction.

The current–voltage (I–V) characteristics of the Si-doped cBN samples with Silver paste electrodes on the top and bottom surfaces were measured at the temperature range of 300–500 K by using a Keithley 2410 SourceMeter. The activation energy of the impurity of the cBN samples was also calculated from the dependence of current on the reciprocal of temperature.

Please cite this article in press as: X. Li, et al., Investigation on cubic boron nitride crystals doped with Si by high temperature thermal diffusion, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.059