Study on the Effect of Phosphorus Doping on Nano-SiC Structure

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Abstract. The short-wavelength emission of nano-silicon carbide has long been confirmed. It is an ideal material for making short-wavelength light-emitting and optoelectronic devices. However, due to the relatively large band gap of silicon carbide, it is generally greater than 2eV. In the ideal case of chemical ratio, the energy band formed by the outer electrons of the atom is full, the conduction band is empty, and the Fermi energy level is in the forbidden band. In this paper, n-type nano-SiC films are prepared by P in-situ doping technology, and the structure of n-type silicon carbide with different doping ratios is analyzed.

Keywords: nano-silicon carbide; structure; doping ratio.

1. Introduction

At room temperature, the electrons in the valence band cannot be thermally excited to cross the wider forbidden band. As long as the external electric field is not particularly strong, theoretically there should be no freely moving carriers, so it appears as an electrical insulator (resistivity is 1012Ω.cm). Because optoelectronic applications usually require a small contact resistance between the device and the circuit, the intrinsic SiC film itself cannot be used for light-emitting and optoelectronic devices. Doping is an indispensable process for SiC to move toward devices. Many different doping techniques have appeared in the research process of silicon carbide doping process: diffusion doping, ion implantation doping, in-situ doping, etc. In-situ doping is a doping technology compatible with the large-scale integrated circuit CVD process. The dopant gas can be directly mixed with the source gas, so it is easy to implement. There are many choices of doping gas, and the doping effects of different doping gases are also different. Both P and N are optional impurities for n-type doping of SiC. Studies have shown that P doping can be higher than N doping. Higher saturated free carrier concentration.

The phosphorus dopant used in the experiment is phosphane (PH3). In order to study the influence of doping gas ratio on the structure and photoelectric properties of the film, n-type nano-silicon carbide films with different PH3 doping ratios (PH3: SiH4) were prepared. And its structure, morphology, optical and electrical properties were characterized.
2. Infrared spectrum analysis of different proportions of doping

In order to analyze the bonding configuration in the film, in this experiment, we used the Bio-Rad 60V Fourier Transform Infrared Transmission Spectrometer to measure the infrared transmission of the deposited samples. The wavenumber range is 400-4000 cm\(^{-1}\), and the resolution is 4 cm\(^{-1}\). Figure 1 shows the infrared transmission spectra of SiC films with different phosphorus doping ratios. The main features in the figure show the bands related to Si-C absorption, especially the absorption band around 800 cm\(^{-1}\). This is under different doping conditions. The intensity and half-width of an absorption band do not change much. With the increase of the doping ratio, the intensity and half-width of the absorption band increase slightly. By fitting this peak, we can calculate the crystallinity of nano-silicon carbide in the film. It is about 60%, and we found that the crystallinity of the film increases with the increase of the doping ratio. In contrast, the infrared absorption peak of single crystal SiC generally appears near 795 cm\(^{-1}\), while the infrared absorption of amorphous silicon carbide generally appears at 740 cm\(^{-1}\). For nano-SiC due to the quantum confinement effect, the particle size is small, which usually causes this absorption peak to be blue-shifted, which shows that the film under this condition is nc-SiC with high crystallinity. This weak shoulder at approximately 1000 cm\(^{-1}\) can be attributed to the Si–CH \(_n\) rocking pattern. The band at about 2100 cm\(^{-1}\) is related to the Si–H \(_n\) (n=1, 2, or 3) bond stretching mode. We noticed that this peak shifts slightly to the higher wavenumber direction with the increase of the doping ratio. This shift is generally due to the change of C content, this mode is generally at 2000 cm\(^{-1}\) in amorphous silicon carbide, while it generally moves to 2100 cm\(^{-1}\) in SiC. This movement is caused by the surrounding C environment, if it is higher, the presence of a proportion of C will make this mode move to a higher wave number. The slight movement here may be due to the slight increase in the C content in the film. This effect will be related to the doping mechanism of P. P can replace the C in SiC at a higher doping ratio, causing a slight increase in the C content. Finally, the absorption band at approximately 2800–3000 cm\(^{-1}\) corresponds to the C–H \(_n\) bond stretching mode of sp\(^3\).

![Figure 1. Infrared spectra of different P-doped nc-SiC films](image-url)
3. Raman spectrum of doped nano-silicon carbide film

Raman spectroscopy, as a supplement to infrared spectroscopy, is often shared with infrared spectroscopy. Raman spectroscopy is composed of those vibrations that do not cause changes in molecular dipole moments, that is, information about infrared inactive vibrations. Compared with infrared spectroscopy, Raman spectroscopy is less affected by factors such as film thickness and substrate. Although SiC films are also Raman active, many experimental results show that in the Raman spectra of SiC films prepared by various techniques, a strong C-C is often found in the range of 1300-1600 cm\(^{-1}\), there are also Si-C (TO) transverse optical mode vibration absorption peaks found at 790 cm\(^{-1}\) and Si-C (LO) longitudinal optical vibration mode found at 970 cm\(^{-1}\).

![Raman spectrum of undoped and phosphorus-doped SiC with a ratio of 1%](image)

Figure 2. Raman spectrum of undoped and phosphorus-doped SiC with a ratio of 1%

Figure 2 shows the Raman spectra of low-doped and undoped SiC samples. It can be seen that there are four broad Raman vibration bands around 470, 775, 940, and 1350 cm\(^{-1}\). The strong Raman band around 470 cm\(^{-1}\) mainly comes from the scattering of amorphous silicon. In addition, the acoustic mode of amorphous SiC may also contribute to it; the broad peak at 1350 cm\(^{-1}\) comes from the scattering of amorphous graphite-like CC clusters. The scattering intensity of samples higher than 1% doped is weaker, which shows that the content of impurity C is small. This result can be explained as P mainly replaces the Si atoms in SiC under the condition of low doping ratio, so the increase of P doping mainly leads to the relative content of C in the film decreases. There are two sharp peaks near 775 cm\(^{-1}\) and 940 cm\(^{-1}\) in the Raman spectrum. Corresponding to the crystalline 6H-SiC transverse optical phonon mode (TO) and longitudinal optical phonon mode (LO) respectively. The appearance of the scattering peaks of these two modes indicates that there are SiC crystals inside the sample. It can be seen from the figure that the two spectral peaks have asymmetrical broadening and red shift relative to the bulk crystalline SiC Raman peak. This result can be attributed to the quantum confinement effect of the smaller SiC grains in the film. Comparing the results of (a) and (b) in Fig. 2, it can be seen that the intensity of the scattering peak of SiC nano-SiC with low doping ratio and undoped film increases compared with that of undoped film. This result shows that doping increases the crystallinity of the film.
4. Surface morphology of doped nano-SiC

Figure 3 shows the surface morphology of the sample with 1% doping. It can be seen from Figure 3(a) that the film contains nanoparticles with a higher density. The average size of the particles is about 20nm. It is also found that there are many sizes in it. For smaller particles and slightly larger nanoparticles, in order to more clearly determine the crystal type and structure of the particles, Figure 3(c) shows the SEM of the sample under the same conditions. The clear scanning electron microscope shows that the sample contains many triangles. These results show that the nano-SiC particles are 6H-SiC with hexagonal crystal structure.

5. Conclusion
In this paper, by changing the ratio of dopant gas and source gas, nano silicon carbide films with different doping and structures are obtained. By analyzing the infrared and absorption spectra, we believe that the main doping mechanism is substitutional doping, that is, the substitution effect of P atoms on Si and C. In the case of lower doping, it is mainly to replace the Si in it, and with the doping the increase in the ratio will replace the C atoms. And as the doping ratio increases, the crystallinity of the film increases. The height and width of the interface barrier decrease, which is manifested as the
photoluminescence intensity of the film increases by an order of magnitude as the doping ratio increases.

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