Epitaxial growth of Ge film on 6H-SiC(0001) by LPCVD

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Ge thin films were prepared on 6H-SiC(0001) substrates by low-pressure chemical vapor deposition. X-ray diffraction, Scanning electron Microscope and Raman spectroscopy were applied to characterize the Ge/6H-SiC heterostructures. XRD spectra shows that only one peak is located at 2θ=26.68°, which indicated that Ge films grow preferentially along <111> crystalline orientation on 6H-SiC(0001) Si-face at 850℃. The epitaxial growth of the Ge film follows the Stranski-Krastanow mode, Ge spherical islands form on the two-dimensional layer with a critical thickness of 7.5nm.

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1. Introduction

SiC semiconductor materials have attracted considerable attention because of its wide applications for various optoelectronic and electronic devices. However, SiC is not sensitive to long-wavelength lights ranging from visible to the infrared region due to its wide bandgap [1-6]. A promising way to solve this problem is to adopt a SiC/Ge heterostructure, in which Ge material can be use as the near-infrared light absorption layer for its high absorption rate and high electron mobility. The SiC/Ge heterostructure can be used to develop the SiC-based devices applications in the near-infrared photoelectric field. However, the epitaxial growth of the SiC/Ge heterostructure is rarely reported [7, 8]. A. Bouzidi et al. simulated the photocurrent density of a n-6H–SiC/p-Si/n-Si/p-$Si_{0.8}Ge_{0.2}$ multilayer solar cell, and the ideal photocurrent increased 15% compared with the same structure of n-p-n-p type Si solar cells. This demonstrated the application possibilities of the SiC/Ge heterostructures in infrared optoelectronics [7], however the SiC/Ge heterostructures have not been prepared. A. Perez Tomas et al. prepared n-n SiC/Ge heterojunction by using MBE method. The electrical performance of the n-n SiC/Ge heterojunction is excellent. However, the growth method is different and the photoelectric characteristics of the SiC/Ge heterojunction are not studied.

In this paper, the 6H-SiC/Ge heterostructures are prepared by using low pressure chemical vapor deposition (LPCVD) on 6H-SiC substrates [8], the epitaxial growth mode of the 6H-SiC/Ge heterostructures is characterized.

2. Experimental

SiC/Ge heterostructures were prepared on on-axis 6H-SiC(0001) Si-face by LPCVD at different growth temperatures. Germane (GeH_4) and hydrogen (H_2) were used as the source and the carrier gas respectively, and the H_2/GeH_4 ratio is equal to 200:20sccm. 6H-SiC substrates were cleaned by the standard RCA method prior to deposition, then treated in H_2 atmosphere at 1050°C for 10min. The growth time is 90min, the chamber pressure is about 440Pa and the growth temperature is 825 ℃ ~875 ℃ . The crystalline orientations of the Ge films on 6H-SiC substrates were characterized by X-ray diffraction (XRD, SHIMADZU XRD-7000). The surface and interface morphologies of the heterostructures were analyzed by scanning electron microscopy (SEM, JSM-6700F). Raman Spectroscopy (RENISHAW inVia) were performed on the samples using 514.5nm laser excitation and the space resolution of Raman spectroscope is $1cm^{-1}$, was also used to characterize the epitaxial films.

3. Results and discussion

3.1. The influence of temperature on the Ge films

Fig. 1 shows XRD data of the Ge film on the 6H-SiC substrate with different growth temperature. Several intense XRD peaks are clearly observed, which are located at 2θ=26.68°, 2θ=45.38°, 2θ=53.76°and 2θ=61.32°. According to the database of joint committee on power diffraction standards, these XRD peaks represent Ge(111), Ge(220), Ge(311) and Ge(400), respectively. When the growth temperatre is 850℃, the SiC/Ge heterostructure has only one XRD peak located at

2θ=26.68°, which belongs to Ge (111) plane. It is demonstrated that Ge films on 6H-SiC have polycrystalline structure with <111> preferred orientation at 850℃. The Ge (111) peak located at 2θ=26.68° exist in all samples prepared at 825~875°C. With the increase of the growth temperature, the (111) peak has the narrower full width at half maximum (FWHM) and stronger relative intensity. This demonstrates that the Ge films have higher crystal quality as the growth temperature increases.

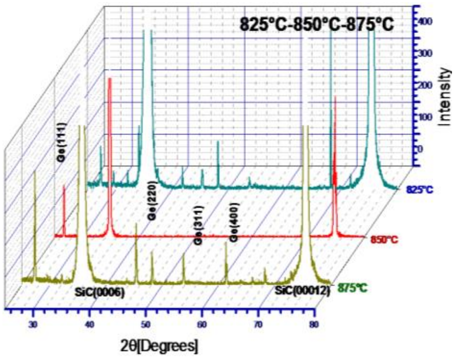

Fig. 1. X-ray specular θ-2θ scans for Ge/6H-SiC(0001) heterostructures with different growth temperatures

The SiC/Ge heterostructure grown at 850℃ is also characterized by Raman spectroscopy, as shown in Fig. 2. There is one Raman peak located at 298.7cm^{-1}, which is corresponding to the TO phonon mode of Ge. This illustrates that Ge films grow epitaxially on 6H-SiC substrate. However, compared with the standard peak of 300.5cm^{-1}, the vibration energy reduced comparatively, and there exists a slight red-shift. Corresponding the vibration modes of Ge, illustrated that the films is Ge indeed. Furthermore, the Raman peak located at 789.5 cm^{-1}, 966.5 cm^{-1} and 1528.0 cm^{-1}, which are correspond to the LO and TO phonon modes of the 6H-SiC substrates, respectively.

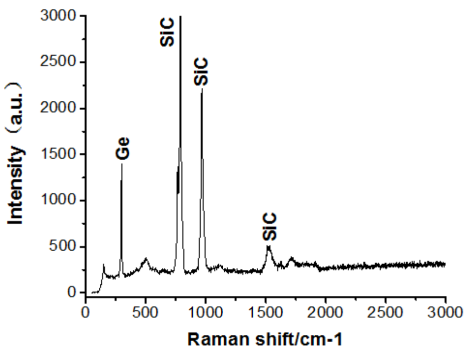

Fig. 2. Raman spectra of the Ge/6H-SiC heterostructure grown at 850 ℃

3.2. The epitaxial modes of the Ge film

As is well known, there are three epitaxial growth modes of heterostructure, Frank-van der Mere (F-M), Stranski–Krastanow (S-K) and Volmer-Weber (V-W) mode. Due to the increase of the strain energy of the epitaxial layer, the two-dimensional (2D) layer growth is no longer the lowest energy state after a certain thickness, and the layer growth turn to the 3D island growth, which is the S-K growth mode. SEM is employed to characterize the epitaxial mode of the SiC/Ge heterostructure. Fig. 3 shows SEM image of the Ge film grown on 6H-SiC substrate at 850℃. Ge thin film exhibits a large number of spherical grains with heterogeneous grain size of 0.3~1.0μm, as shown in Fig. 3(a) and Fig. 3(b). Fig. 3(c) and Fig. 3(d) show the cross-sectional SEM images of the SiC/Ge heterostructure. The SiC/Ge interface is smooth and sharp. It is clearly observed that there is a 2D layer with a critical thickness of 7.5nm between the Ge spherical grains and 6H-SiC substrate. This demonstrates that the epitaxial growth of the Ge film follows not the V-W mode but the S-K mode (2D to 3D mode).

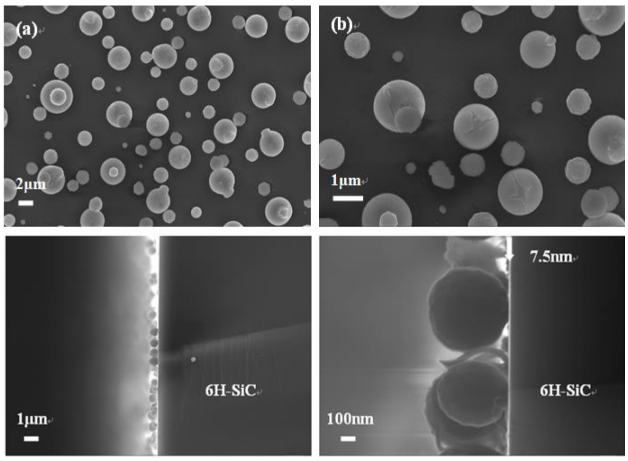

Fig. 3. SEM images of Ge films grown on 6H-SiC substrate at 850 ℃. (a, b) surface SEM images, (c, d) cross-sectional SEM images

Although the island growth mode was observed in Ge films, the idiographic growth state is still unclear. The nucleation and initial growth are the important stages of the island growth, and are also the important periods to investigate the growth mode and the interior structure; therefore the island formation of the Ge films is also observed, as shown in Fig. 4. At the initial growth stage, a large number of cores with different sizes are formed on the Ge film surface. Due to the lowest free energy trend, small cores evaporate spontaneously, meanwhile the large ones absorb the evaporated Ge molecules under the low equilibrium vapor, therefore the small cores gradually disappear and the large cores grow up. This is the Oswald coalescence, and the process can be clearly observed in Fig. 4. Furthermore, there are crystalline whiskers around the nucleus, which is a highly ordered atomic structure. It demonstrates the existence of single crystal thin films on flat surface after the coalescence of crystal cores.

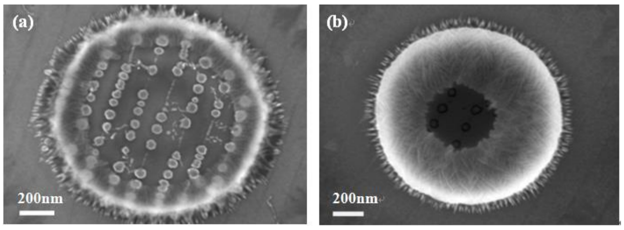

Fig. 4. SEM images of the Ge film on 6H-SiC surface. (a) initial stage of the Ge grain coalescence, the growth time of the Ge film is 90 min, (b) later stage of the Ge grain coalescence, the growth time is 120 min

4. Conclusions

In this paper, Ge thin films were prepared on 6H-SiC(0001) substrate by LPCVD. XRD, SEM and Raman spectroscopy were used to characterize the morphologies and the crystalline structure. It is shown that Ge films grow preferentially along <111> crystalline orientation on 6H-SiC(0001) Si-face at 850℃. The epitaxial growth of the Ge film follows the S-K growth mode, Ge spherical islands form on the 2D layer with a critical thickness of 7.5nm.

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