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Raman investigation of different polytypes in SiC thin films grown by solid-gas phase epitaxy on Si (111) and 6H-SiC substrates

J. Wasyluk[1,a], T.S. Perova[1,b], S.A. Kukushkin[2,c], A.V. Osipov[2,d], N.A. Feoktistov[3,e], and S.A. Grudinkin[3,f]

[1]Department of Electronic and Electrical Engineering, University of Dublin, Trinity College, Dublin 2, Ireland

[2]Institute of Problems of Mechanical Engineering, Russian Academy of Sciences IPME RAS, Bolshoy 61, V.O. St. Petersburg, 199178, Russia

[3]Ioffe Physico-Technical Institute, Polytechnicheskaya ul., 26, St.-Petersburg, 194021, Russia

[a]wasyluj@tcd.ie, [b]perovat@tcd.ie, [c]ksa@math.ipme.ru, [d]osipov@ineos.ac.ru, [e]Feokt@gvg.ioffe.rssi.ru, [f]grudink@gvg.ioffe.rssi.ru

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Abstract. Raman spectroscopy was applied to investigate a series of SiC films grown on Si and 6H-SiC substrates by a new method of solid gas phase epitaxy. During the growth characteristic voids are formed in Si at the SiC/Si interface. Raman peak position, intensity and linewidth were used to characterize the quality and the polytype structure of the SiC layers. A large enhancement in the peak intensity of the transverse optical and longitudinal optical phonon modes of SiC is observed for the Raman signal measured at the voids. In addition, scanning electron microscopy and atomic force microscopy were used to investigate the surface morphology of SiC layers.

Introduction

Silicon carbide (SiC) is a promising wide band gap semiconductor for high-power, high frequency and high temperature devices, due to its breakdown field, high electron saturated drift velocity and good thermal conductivity [1]. Besides, 3C-, 4H- and 6H-SiC are also attractive materials to be used as a substrate for GaN and AlN blue light-emitting diodes (LEDs) [2]. Therefore, the reproducible growth of one or another SiC polytype on silicon wafer is nowadays a very important issue for the semiconductor and MEMS industry. At present mainly two methods exist for deposition of SiC on Si substrate: molecular-beam epitaxy (MBE) [3] and chemical vapour deposition from the gas state [4]. None of these provide yet the possibility of growth of very good quality SiC substrates for use in power electronics or as a buffer layer for growth of high quality GaN.

SiC has over 170 different polytypes [5]. The most common forms are 4H, 6H known as the hexagonal (α-SiC) types, and cubic (3C-SiC) type [5-8]. The building units of all polytypes result from different stacking in the SiC double layer [6]. Raman scattering is a powerful and non-destructive tool, which can be used in identifying the polytype structure of SiC as well as for stress and defect analysis. In the case of 3C-SiC two strong Raman peaks are observed, one at 972 cm^{-1} that is assigned to the longitudinal optical (LO) phonon peak, and another at 796 cm^{-1} assigned to the transverse optical (TO) phonon peak [8]. Hexagonal modes for 6H-SiC are indicated by splitting the TO mode into three peaks: TO_2 at 767 cm^{-1} and 789 cm^{-1}, TO_1 at 797 cm^{-1}, and one LO_1 mode at 965 cm^{-1} [8].

In this work, different polytypes in SiC thin layers grown by a new method of epitaxy were investigated using Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive X-ray analysis (EDX).

Experimental

A series of SiC films with thickness varying from ~200nm up to 1μm and with different polytype structure (3C, 6H, 4H) were grown on Si (111) by a new method of solid gas phase epitaxy, resulting in the formation of voids in the Si substrate near the SiC/Si interface [9]. The deposition of SiC is achieved by means of the chemical interaction between mono-crystalline Si and CO in gas phase. Some silicon atoms transform into gaseous SiO and diffuse from the substrate, which leads to the formation of vacancies and voids in Si [9]. Due to the fabrication procedure, these samples are lightly doped mainly with nitrogen at the level of 10^{14} cm^{-3}.

The micro-Raman scattering measurements were carried out at room temperature in the backscattering geometry using a RENISHAW 1000 micro-Raman system equipped with a CCD camera and a Leica microscope. An 1800 lines/mm grating was used for all measurements, providing a spectral resolution of ~ 1 cm^{-1}. As an excitation source, an Ar+ laser at 457 nm with power of 10 mW was used.

The surface morphology of SiC was examined by Tescan Mira SEM and by NT-MDT AFM operating in contact mode. The quality of the crystalline structure was investigated by EDX analysis.

Results and discussion

Results of Raman analysis of two samples with SiC film grown on Si (111) and 6H-SiC substrates are presented in this work. Raman spectra of bulk 6H-SiC substrate as well as 3C-SiC layer grown on 6H-SiC substrate, measured with 457 nm of excitation wavelength, are shown in Fig. 1. For bulk 6H-SiC three characteristic features are observed: the LO phonon mode with A_1 symmetry at 965 cm^{-1} and two TO phonon modes at about 788 and 766 cm^{-1} with E_2 symmetry. This is in agreement with previously published data [8,10,11]. For sample with SiC layer grown on 6H-SiC substrate two additional bands, corresponding to 3C-SiC, were observed: TO phonon mode at ~796 cm^{-1} and low intensity LO phonon mode at ~978 cm^{-1} on the left side of LO 6H-SiC peak. Figure 2(a) shows Raman spectra of SiC film, grown on Si substrate, measured with 457 nm of excitation wavelength at the void and outside the void. As seen from Fig. 2(a) the cubic 3C-SiC characteristic modes of TO and LO phonons appear at 794 cm^{-1} and at ~ 968 cm^{-1} respectively. This confirms that the SiC layers, analyzed in this work, consist mainly of cubic polytype structure [8,12]. We note that the peak at 794 cm^{-1} can also be attributed to TO phonon mode for disordered 6H-SiC structure observed for back scattering configuration. However, this peak is significantly low intensity compare with another TO peak observed in 6H-SiC at 788 cm^{-1} (see Fig. 1). This exclude an assignment of the peak at 794 cm^{-1} to the 6H-SiC polytype. A low intensity shoulder observed at ~ 764 cm^{-1} near the TO band indicates the presence of small amount of 4H-SiC polytype in this SiC layer. The wide feature seen in the range 900-1010 cm^{-1} is associated with Si second-order Raman scattering [13]. This peak is overlapped with LO phonon peak of SiC layer, which complicates the use of LO peak position for drawing the conclusion on SiC structure. The large enhancement of the Raman peak intensity for both TO and LO modes is observed in the void area. This can be explained by multiple internal reflections of the laser light beam inside the void. A similar effect was discussed for porous SiC in Ref. [14] and for porous Si in Ref. [15]. Additionally, the voids are partly filled with SiC material, which can also influence on enhancement of Raman signal. In accordance to Nakashima paper [8], the structural disorder in SiC leads to the symmetrical widening of all TO peaks. In case of spectra shown in Fig. 2(b), the 3C-SiC TO peak shows the asymmetry from low-frequency side only. We conclude that this asymmetry is due to the presence of 6H-SiC peak at ~789 cm^{-1}, which is clearly demonstrated by fitting of TO band (see Fig. 2(b)). From the fitting the linewidth of band at ~794 cm^{-1} is determined to be approximately ~7.8 cm^{-1}. This is only 2.5 cm^{-1} larger than for relaxed 3C-SiC on 6H-SiC substrate shown in Fig. 1. This relatively small difference in linewidth leads to the conclusion that thin SiC layer grown on Si (111) has a

reasonably good crystalline quality. This is also confirmed by electron diffraction pattern (see Fig. 3(c).) Almost no circles characteristic of the polycrystalline phase are seen on Fig. 3(c), but there are well-defined Kikuchi lines, which indicates that the crystal structure of the film is of good quality [9]. It was shown by numerous x-ray diffraction and electron diffraction studies and luminescence analysis that either the hexagonal or cubic polytype structure, or a mixture of them can be grown by using the growth method presented in this paper [9]. Therefore, we can conclude that the SiC film grown on Si (111) has 3C-SiC structure with the presence of small fraction of hexagonal polytypes. It was also experimentally demonstrated that quality of GaN layers grown on SiC layers with a mixture of cubic and hexagonal polytypes is better than on single polytype of SiC [16].

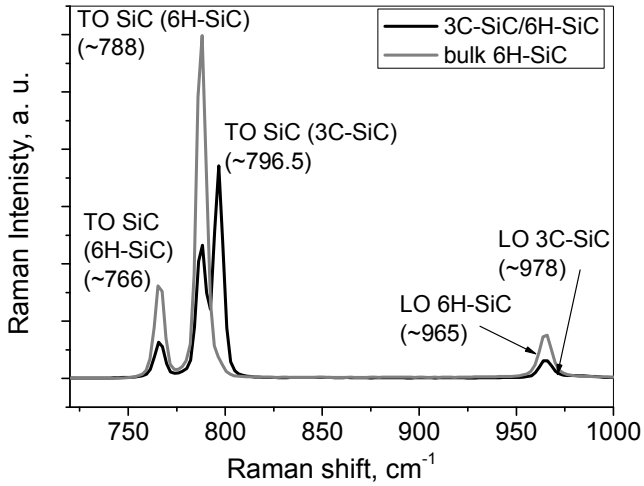

Fig. 1. Raman spectra of bulk 6H-SiC and 3C-SiC layer on 6H-SiC substrate.

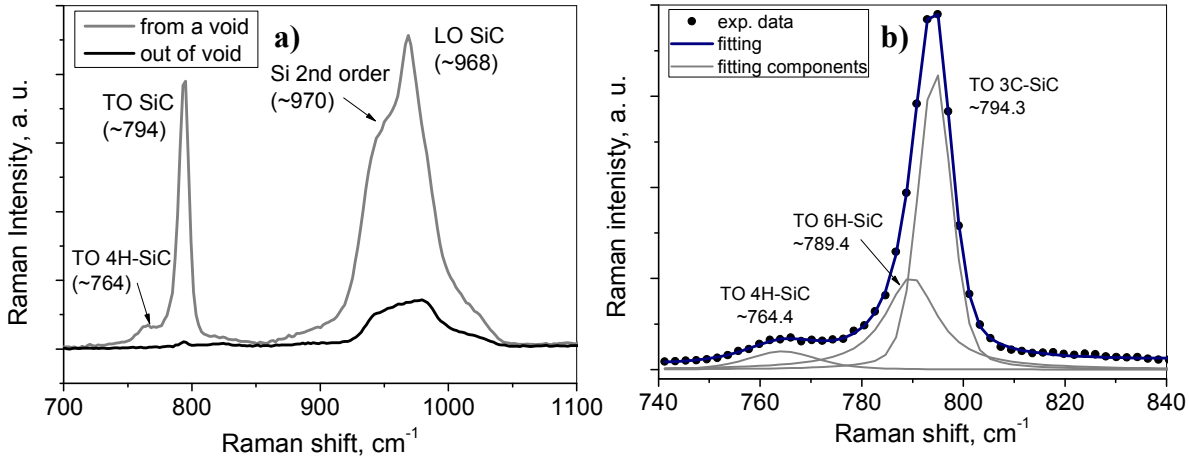

Fig. 2. (a) Raman spectra of SiC layer grown on Si substrate measured at the void area and from outside the void area. (b) Fitting of TO-band spectrum, detected at the void, with three functions (Lorentzian + Gaussian).

The surface morphology of 3C-SiC layer on Si (111), investigated by SEM and AFM microscopy, is demonstrated in Fig. 3(a) and Fig. 3(b), respectively. The triangular grain structure characteristic for 3C-SiC grown on Si (111) is observed, which is in agreement with previously published data [17]. The AFM image analysis reveals the surface roughness of about 15 nm rms.

Summary

The thin SiC layers grown by a new method of solid-gas phase epitaxy were investigated by Raman spectroscopy, SEM, AFM and EDX techniques. It is shown that the SiC layer on Si (111)

investigated here is composed of the cubic polytype of SiC with a small presence of 6H- and 4H-SiC. The presence of the voids has been experimentally confirmed by micro-Raman spectroscopy. The strong enhancement in the peak intensity of the TO and LO modes is observed for the Raman signal measured in the void area. This enhancement of the Raman signal is advantageous as it allows micro-Raman measurements to be used for the detection of different polytypes in very thin SiC layers. The formation of voids leads to the growth of thin SiC layers with low stress and a good crystalline quality. Triangular grain surface structure was observed for the investigated 3C-SiC layer grown on Si (111).

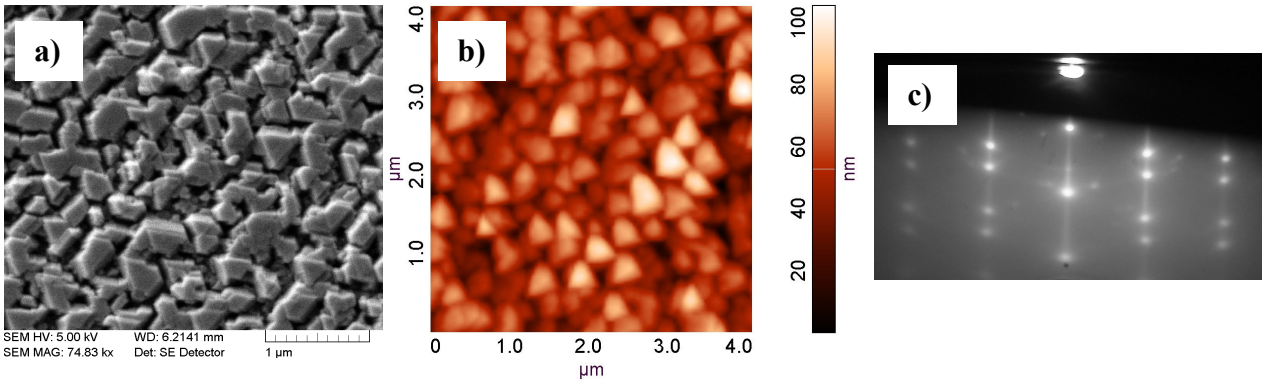

Fig. 3. (a) SEM and (b) AFM images of the 3C-SiC layer grown on Si (111). (c) Electron diffraction pattern of 3C-SiC layer on Si (111).

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