Ion beam induced modification and nanostructures formation in thin SiC/Pd films on c-Si substrate

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A B S T R A C T

Ion beam induced modification of thin metallic films is an emerging approach to grow metallic nanoparticles controllably. Modification of thin solid films is helpful in fabricating arrays of nanoscale particles for electronic and photonic devices and for the catalyzed synthesis of nanotubes and nanowires. In this work, the modification and nanostructures formation over the surface of SiC/Pd thin films of 15 and 45 nm thicknesses, grown on crystalline Silicon (c-Si) substrate by electron beam deposition, upon ion irradiation, have been investigated by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Rutherford back-scattering spectrometry (RBS), Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. The SiC/Pd bilayer films were irradiated with 100 keV Ar$^+$ ions at fluences of 1×10^{15} and 5×10^{15} ions/cm^2 at room temperature. The surface morphology from SEM analysis showed the formation of nanoparticles that were interconnected after irradiation. The RBS and EDS results confirmed the presence of Pd, C, O and Si. While the Raman spectrum of the pristine sample displayed only a sharp peak at 520 cm^{-1} characteristic to c-Si substrate, the spectra of the irradiated sample red-shifted to lower wavenumbers indicating the appearance of Si nano-crystals.. Hence, ion beam irradiation is a promising method for the fabrication of SiC nanostructures on c-Si substrate.

1. Introduction

Ion beams have been used for the synthesis and modification of materials over the past decades. Ion beams with energies in the keV range have been used for surface modification through ion implantation. Thus, ion beam modification of materials uses energetic ions with a broad range of energies for modification of electrical, optical, structural and chemical properties of materials [1]. Recently, it has been shown that ion beams can cause surface modification of metal films on non-reactive substrates which can lead to a patterned surface [2–4]. The growth of metallic nanoparticles from thin films offers the possibility of scientific insight into novel processes [5] and advantages in development due to the adaptation of existing thin film technology. SiC is known for its outstanding properties such as wide band gap, high-temperature stability and high thermal conductivity, radiation hardness and chemical inertness [6,7]. These properties make SiC a material of choice for applications in semiconductor devices which are operated in extreme conditions of temperature, power and irradiation [8]. Several methods

have been employed to synthesize SiC nanostructures, such as sol–gel [9], atomic layer deposition (ALD) [10], chemical vapour deposition (CVD) [11], and electron beam evaporation [12]. Among these techniques, ion beam irradiation with beams in the tens to hundreds of keV range has been utilized to induce modification of metal thin films in order to grow nanostructures at room temperature [13,14]. Lee et al. [15] have observed some intermixing of palladium films with silicon after implanting with phosphorus ions. Moreover, van der Weg et al. [16] have noted interdiffusion of Pd/Si after implanting with Ar$^+$ ions. They observed no bubbles after implantation with Ar at high ion fluence whereas He bubbles were noted after implantation at the same ion fluence. There is a lot of literature on the effects of ion beam irradiation of metal thin films on substrates [15,17,18]. To our knowledge, there has been no or little focus on the effect of ion beam modification of a thin metal layer sandwiched between a thin semiconductor film and the substrate. In this work, ion beam modification and nanostructures formation in SiC/Pd thin films stacks of 15 and 45 nm thicknesses, grown on crystalline Silicon (c-Si) substrate by electron beam deposition, upon

ion irradiation have been investigated by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Rutherford backscattering spectrometry (RBS) and Raman spectroscopy.

2. Experimental details

Pd metal catalysts of about 5 nm thickness were deposited on c-Si (1 0 0) substrates by electron beam evaporation. Then, SiC thin films of thicknesses 10 and 40 nm were deposited in situ on the Pd/Si (1 0 0) layered structure. Prior to the deposition, the substrates were cleaned in an ultrasonic bath using acetone, methanol and deionized water in sequence for the duration of 10 min for each step in order to remove dirt and contamination. The native oxide layer on the Si substrate was removed by dipping the substrate into 5% hydrofluoric acid (HF) for 1 min. 3C - SiC hot-pressed granules and Pd pellets (Purity 99.99%) targets were placed in the crucibles for the deposition of SiC and Pd thin films. The SiC and Pd samples were deposited at rates ranging between 0.4 and 0.8 A/s in a chamber previously evacuated at 1×10^{-5} mbar. The film thickness was monitored by the quartz crystal monitor. The deposited thin films were later irradiated with 100 keV Ar^+ ions at fluences of 1×10^{15} and 5×10^{15} ions/cm^2. The ion beam irradiation was carried out at room temperature using the 200-20A2F Varian ion implanter at the iThemba LABS Tandem and Accelerator Mass Spectrometry (TAMS) Department in Johannesburg, South Africa. The ion current for the Ar^+ beam was maintained at 1.0 µA. The surface morphology and elemental composition of the films were examined using a JEOL JSM 7500F SEM operated at 3 kV for imaging and 15 keV for EDS analysis. RBS measurements, on both pristine and irradiated samples were performed using a beam of He^+ ions of energy 2.0 MeV delivered by a 6 MV Pelletron Tandem Accelerator at TAMS. The RBS data were acquired using OMDAQ version 3 software [19]. Raman spectroscopy was carried out using a WITec alpha 300R confocal microscope system using a laser wavelength of 532 nm at a power of ~15.45 mW. The data were acquired using the WITec Control software and were analyzed with the WITec Project. Fourier transform infra-red (FTIR) analysis was conducted using a Shimadzi IR Tracer 100, in the range $400 – 4000$ cm^{-1} for molecular vibrational mode studies. All spectra were background subtracted.

3. Results and discussion

3.1. Surface morphology characterization

The SEM micrographs of pristine and ion irradiated SiC/Pd layer stacks on c-Si substrate are presented in Fig. 1. The pristine samples in Fig. 1(a) and (d) show smooth surfaces with small grains. Fig. 1(b) shows the formation of nanoparticles dispersed throughout the surface. As ion fluence increases to 5×10^{15} ions/cm^2, a formation of isolated and interconnected nanoparticles was observed with a small fraction of surface area coverage as shown in Fig. 1(c). When the thickness of the SiC layer was increased to 40 nm (Fig. 1(e)), only few isolated small nanoparticles were observed on the surface. Increasing the ion fluence to 5×10^{15} ions/cm^2 (Fig. 1(f)), resulted in more nanoparticles. However, the nanoparticles are not as conspicuous as those observed at a SiC/Pd thickness of 10/5 nm. From the results obtained, it was noted that film thickness played a huge role in the formation of nanoparticles.

Energy-dispersive X-ray spectroscopy (EDS) analysis was conducted to determine the chemical compositions of the implanted films on different spots. Two spots were chosen in order to determine the chemical composition on the grown nanoparticles and the blank spot. Fig. 2 shows SEM images and corresponding EDS spectra. The SEM images in Fig. 2(a) and (b) show the inspection fields within which the EDS data were collected. The tabulated results show the elemental composition in the inspection field in atomic percent. The EDS analysis conducted on nanoparticles show the presence of Si, C, Pd and O, with Si and C being the most abundant elements, confirming the formation of SiC nanostructures. The oxygen observed from the EDS analysis could be originating from residual oxygen in the deposition chamber and/or post-oxidation in the samples.

3.2. Rutherford backscattering spectrometry (RBS)

Rutherford Backscattering Spectrometry (RBS) was carried out on pristine and ion irradiated SiC/Pd thin films on c-Si substrate. Fig. 3 shows the backscattering spectrum of the pristine sample compared to those of the irradiated samples at fluences of 1×10^{15} and 5×10^{15} ions/cm^2. A reduction in the Pd peak was noted after irradiation. This could
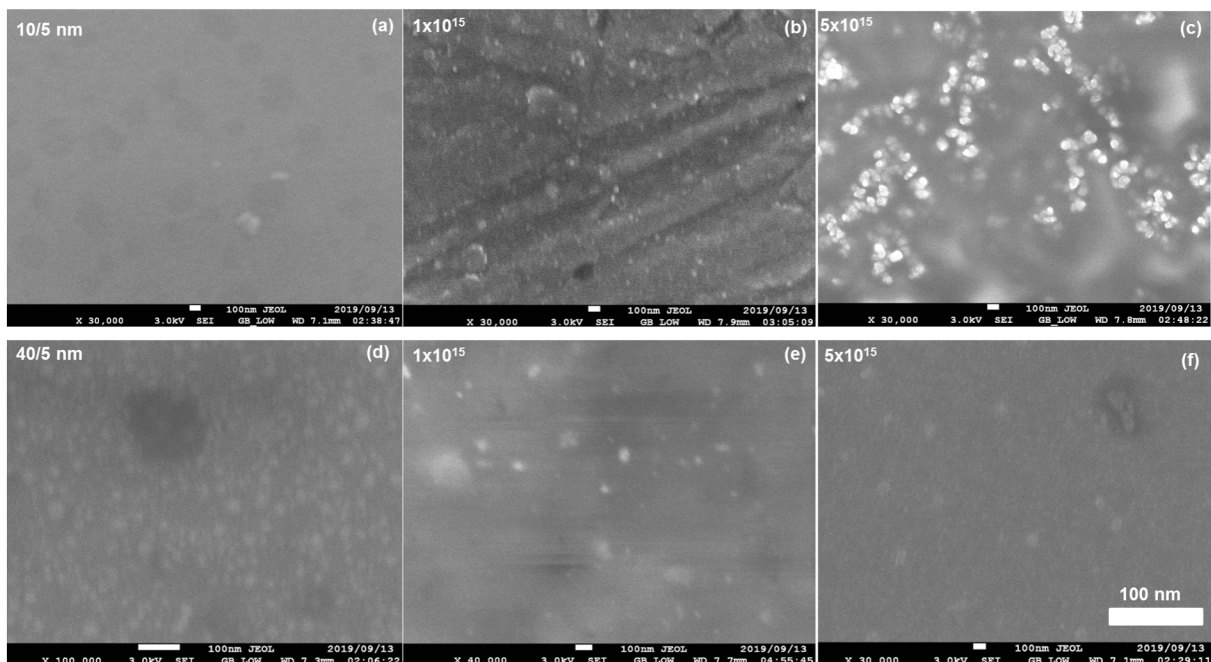

Fig. 1. Top-view SEM micrographs of pristine and irradiated 10/5 nm and 40/5 nm SiC/Pd on c-Si substrate (The 100 nm scale bar appended on Fig. 1(f) applies to all the micrographs).
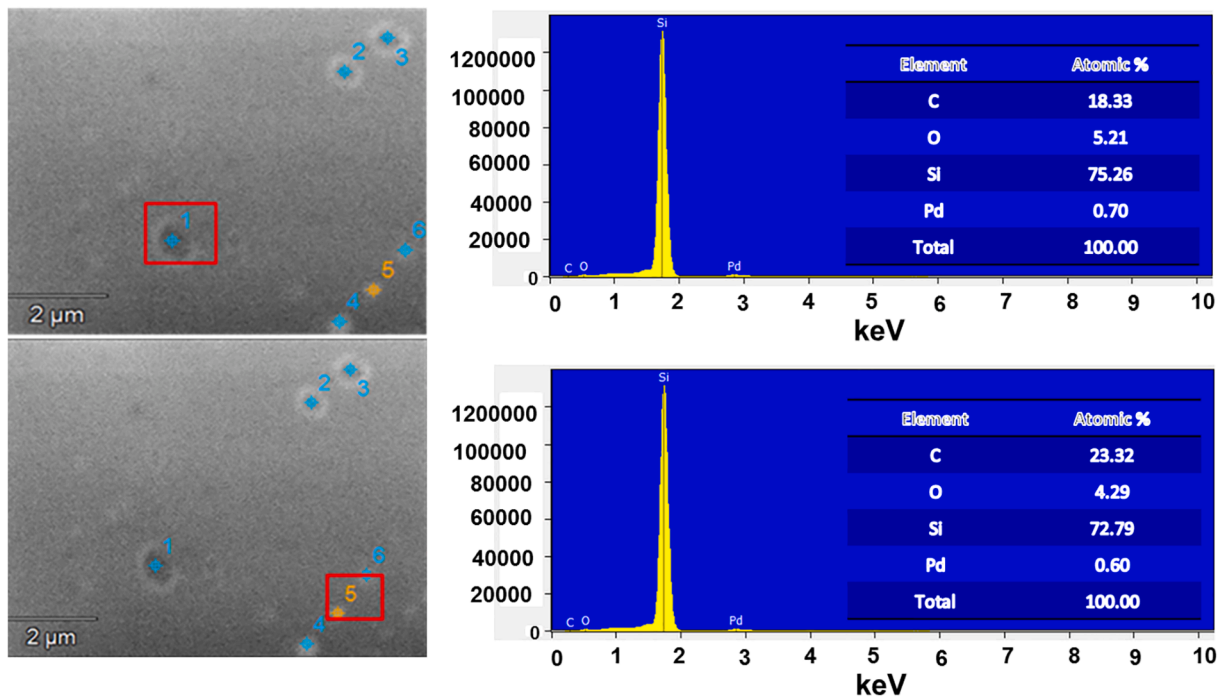
Fig. 2. SEM images and EDS spectra of SiC/Pd on c-Si substrate. The red boxes show the inspection field within which the EDS data were collected. (The probed halo structure is part of an image of a sample irradiated with 1×10^{16} ions/cm^2, which is not shown here). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
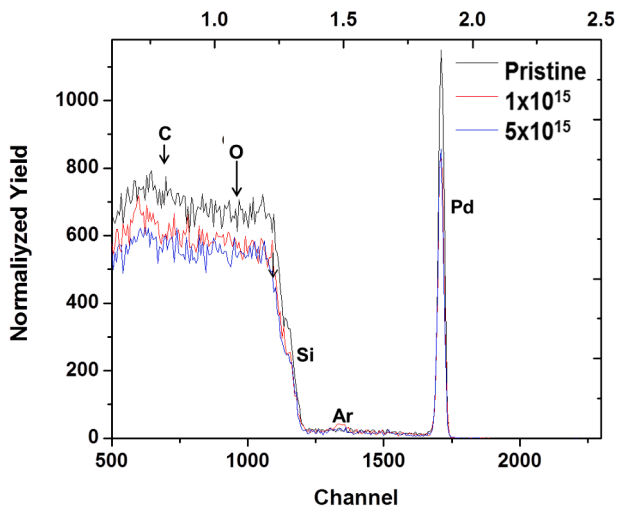

Fig. 3. RBS spectra of 10/5 nm pristine and irradiated SiC/Pd thin films on c-Si substrate.

be due to sputtering. The Pd peak width remained unchanged for the pristine and irradiated samples with no evidence of mixing and diffusion of Pd into SiC and Si substrate. This indicates that the ion beam-induced changes are morphological, with the film forming nanoparticles. This correlates with the SEM results in Fig. 1(b) and (c). The Si edge shows a shift towards the lower energy, indicating the exposure of the substrate from the modification and sputtering. The peak at 1400 keV is due to the embedded Ar$^+$ ions from the incident beam.

3.3. Fourier transform Infrared spectroscopy (FTIR)

The IR transmittances of the irradiated samples were measured using FTIR spectroscopy in order to study the elemental bonding and its evolution with ion irradiation. FTIR spectra of pristine and irradiated

samples at different fluences are depicted in Fig. 4. The IR absorption bands centered around 614 cm^{-1} and 1109 cm^{-1} were noted on both pristine and irradiated samples, which correspond to the Si-Si bond and vibration of asymmetric stretch of the Si–O–Si bond [20 –22]. For the ion irradiated samples, additional absorption peaks emerge at ~736 cm^{-1}, 800 cm^{-1} and 880 cm^{-1} but in a much more pronounced manner in the higher 5×10^{15} ions/cm^2 fluence. The 800 cm^{-1} peak corresponds to the ordered SiC stretching mode and the other two are related to disordered SiC modes. Thus, the absorption band could be due to amorphous SiC precipitates in the sample [23].

3.4. Raman spectroscopy

Raman spectroscopy was employed in order to investigate the formation of SiC nanoparticles in the ion irradiated samples. Fig. 5 shows Raman spectra of pristine and irradiated 10/5 nm SiC/Pd layer stacks on c-Si substrate. The spectrum of the pristine is characterized by a sharp
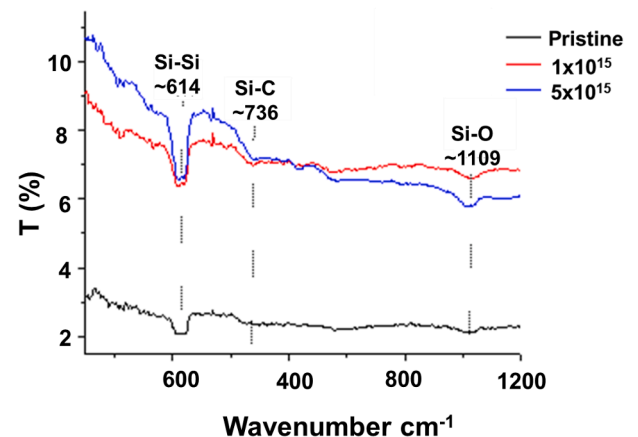

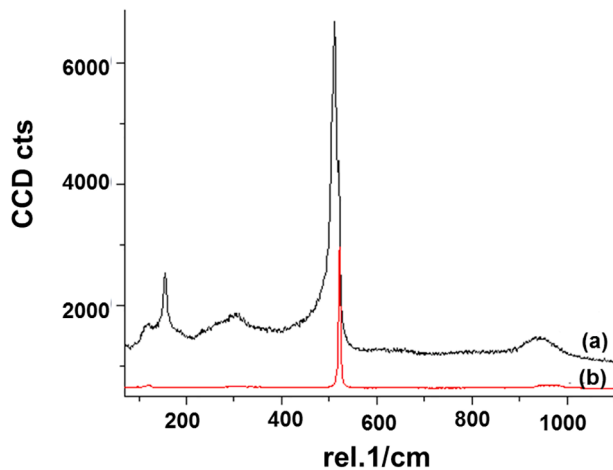**Fig. 4.** The FTIR spectra of 10/5 nm SiC/Pd thin films on c-Si substrate: pristine and irradiated samples at fluences of 1×10^{15} and 5×10^{15}.

Fig. 5. Raman spectra of 10/5 nm SiC/Pd on c-Si substrate (a) pristine and (b) irradiated at ion fluence 5×10^{15} ions/cm^2.

peak centered around 521 cm^{-1} and a broad peak at around 948 cm^{-1} which correspond to the first and second order vibrational modes of Si [24]. The spectrum of the irradiated sample was observed to have broadened and shifted to lower wavenumbers. The broadening of the 521 cm^{-1} peak is attributed to the defects, disorder and nanoclustering induced in the irradiated sample. From the results obtained, there is no evidence of the SiC vibrations in the range $700 - 900$ cm^{-1}. This could be due to the relatively low Raman efficiency for these modes as observed by Brink et al. [25].

4. Conclusions

Nanostructures formation over the surface of thin SiC/Pd films on c-Si substrate by ion beam induced modification with 100 keV Ar$^+$ ions at room temperature has been successfully achieved. SEM studies showed the formation of interconnected grains dispersed throughout the surface of irradiated films at ion fluences of 1×10^{15} and 5×10^{15} ions/cm^2. The SiC thin film thickness was found to be an important parameter on the formation of SiC nanoparticles. SEM images showed that the formation of nanocrystals accelerates with decreasing SiC film thickness. RBS and EDS results confirmed the presence of Pd, C, O and Si. FTIR analysis shows only a prominent Si-Si peak in the pristine sample while the ion irradiation of the films resulted in the rearrangement of atomic bonding

in ordered SiC and in disordered SiC clusters. From the Raman spectral analysis, the pristine sample was characterized by a sharp peak at 521 cm^{-1} due to the c-Si substrate while the effect of the irradiation translated in the red-shifting and broadening of this peak; this was attributed to the formation of defects, disorder and small nanostructures in the ion implanted films.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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