Raman microscopy study of pulsed laser ablation deposited silicon carbide films

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Abstract

Silicon carbide films have been deposited by pulsed laser ablation. The sample microstructure was studied by means of SEM imaging and spatially resolved Raman spectroscopy. Some inhomogeneities, on an otherwise structureless sample surfaces, were evident in the SEM images. A detailed Raman imaging study was carried out over a properly selected area including some inhomogeneous spots. Analysis of the spectral features relative to phonon modes revealed a variety of structural configurations. In the homogeneous region, the amorphous phases of silicon carbide, graphitic carbon and silicon were identified. On the other hand the inhomogeneous spots contained predominantly microcrystalline phases of both silicon and graphitic and/or tetrahedral carbon species. Micro-Raman spectroscopy provided an excellent tool, in giving local structural information by selectively probing a microscopic scattering volume. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Pulsed laser ablation deposition (PLAD) has become one of the most powerful methods to obtain a wide class of materials in the thin film form. The technique is based on the removal of material from a target by means of a collimated beam of high energy laser (excimer, CO_2 or Nd:YAG lasers). The interaction of the laser beam with the target produces a highly oriented material stream, usually ejected normal to target surface that deposits onto appropriate substrates positioned in front of the target. Such a stream consists of neutral and ionized atomic or molecular highly energetic species present in the target. The process, and as a consequence the properties of the deposited films, is strongly dependent on many parameters. Among these the most important are (i) the laser fluence and wavelength, (ii) the structural and chemical composition of the target material, (iii) the chamber pressure and the chemical composition of the buffer gas, (iv) the substrate temperature. By means of a PLAD superconductor YBCO thin films [1], conductive oxides [2], ferroelectrics [3] and also amorphous SiC films have been successfully realized [4,5].

The aim of this work is to investigate the structural properties of amorphous SiC thin films deposited by means of PLAD. In view of the metallurgical and microelectronic technological applications of SiC thin films, this technique is very interesting since the depositing species are very energetic and it is generally possible to obtain well ordered and high density films, also at low substrate temperatures. Nevertheless, one of the major problems typical of the PLAD is the particulate generation. In fact, besides atomic and molecular species some micron and submicrometer sized particles are ejected from the target and included in the film. This causes the presence of structurally inhomogeneous bulk regions and an increased surface roughness, which are undesirable in a large number of technological applications. The most important deposition parameters that affect both the density and the dimensions of such particles are laser fluence and wavelength. Usually the wavelength λ effect is related to the absorption coefficient $\alpha(\lambda)$ of the target, which results in different laser penetration depth as a function of the target material. The larger the penetration depth the higher the density and dimensions of particulates [6]. Laser fluence has a similar influence on particulate generation. Then, surfaces of PLAD thin films could show a non-homogenous structure.

The present study was carried out by means of micro-Raman scattering measurements. This technique demonstrated to be a powerful tool in order to investigate the structural properties of non-homogeneous surfaces of
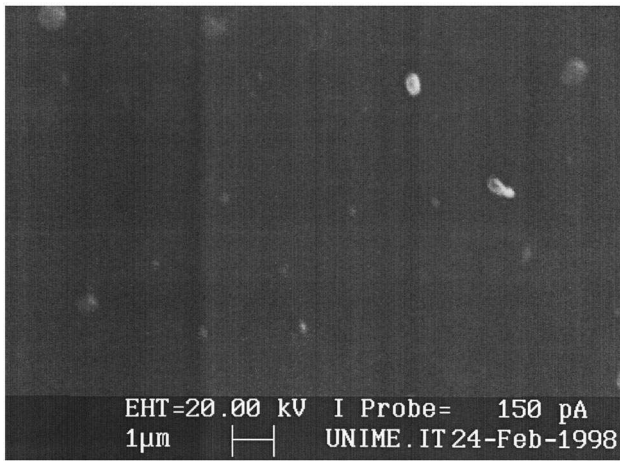
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Fig. 1. Typical SEM image of the surface of a PLA deposited a-SiC film. The surface appears rather smooth with the exception of some micrometer and sub-micrometer sized inhomogeneities.

PLAD thin films, due to its high spatial resolution which allows one to obtain a detailed map of the Raman spectra over a properly selected area. The Raman lines of silicon and carbon are strongly dependent on the structural properties of the samples, in particular both line position and width of the silicon transverse optical phonon mode are strongly dependent on the local order of the silicon network. Raman scattering can be used to investigate the structural arrangement of carbon atoms, being it able to identify both sp^2 and sp^3 carbon configurations. Also local vibrational mode can be detected by Raman scattering in materials lacking of long range order, such in the case of amorphous compounds.

2. Experimental

Films were deposited by ablating a rotating target, made of high purity reaction bonded SiC or crystalline 6H-SiC, using a frequency doubled 532-nm Nd:YAG laser beam focused onto the target. The deposition took place in a high vacuum chamber at pressures better than 1×10^{-6} mbar. The estimated laser spot on the target surface was approximately 2 mm^2, and, each impulse having a energy of 150 mJ and 10 ns duration, the laser fluence was 7.5 J/cm^2. The repetition rate was kept fixed at 20 Hz. Films were deposited, at room temperature, onto 7059 Corning glass and c-Si substrates positioned at 40 mm from the target. Micro-Raman scattering measurements were performed by a Dilor LabRam spectrometer equipped with a Olympus BX40 confocal microscope. A 15-mW He–Ne laser beam was focused by the optics of the microscope onto an area of 0.7 μm on the sample surface. The backscattered radiation
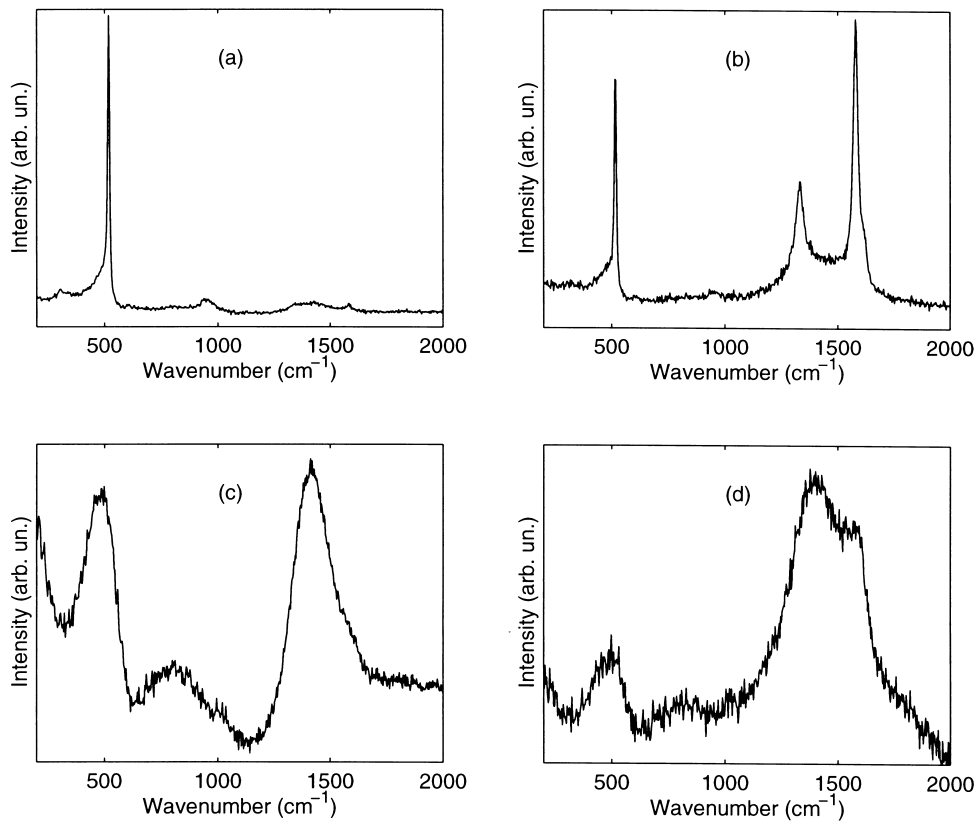

Fig. 2. Raman spectra collected at different sampling points on the surface of a PLA deposited a-SiC film. The spectra are representative of four main different structural arrangements detected over an area of 30×30 μm.
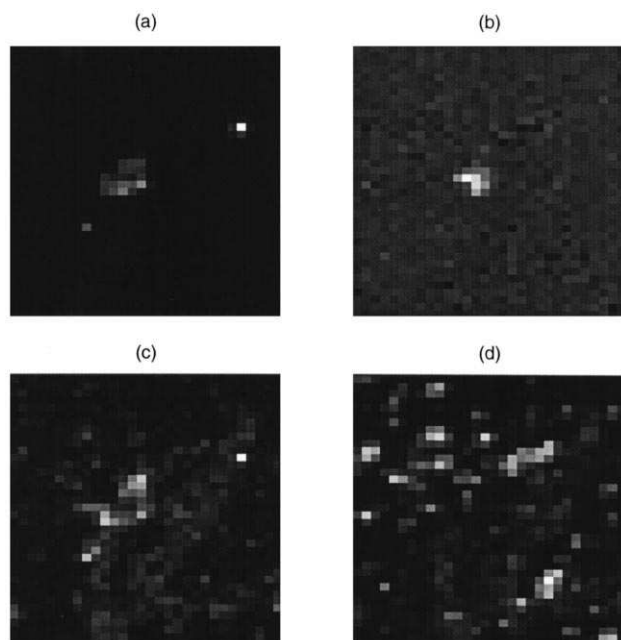
Fig. 3. Map of the 30×30 μm area obtained by integration of a Raman band typical of the spectra shown in Fig. 1. The obtained values are represented on a 255 grays scale. Brighter spots correspond to higher integrated area values.

was collected by the same optics of the microscope and dispersed by a 30-cm monochromator provided with two gratings, which allow investigation in the two spectral ranges 100–1200 cm^{-1} and 150–3100 cm^{-1}, with spectral resolution of 1.0 and 2.5 cm^{-1}, respectively. The elastically scattered radiation was rejected by the use of a notch filter. Finally, a cooled CCD sensor was used to record the spectra, usually averaged for a period of 15 s. The computer controlled stage of the microscope allows movement of the sample with a spatial resolution of 1 μm, then a map of Raman spectra could be recorded over selected area of 30×30 μm. By plotting the intensity of a particular feature of the Raman spectra, i.e. the intensity of the silicon TO phonon mode or the ratio between the crystalline and amorphous silicon contribution, images reproducing these features could be obtained. In such a way a detailed map of the structural properties of a selected area of the sample surface have been constructed. Investigation of samples surfaces were made also by means of a LEO-4300 scanning electron microscope.

3. Results and discussion

In Fig. 1 the SEM image of the surface of the sample, deposited by ablating the reaction bonded SiC target, is shown. As can be seen the surface appears to be rather smooth but some micrometer sized inhomogeneities are also evident. The origin of such inhomogeneous structures has been the subject of several studies (see Ref. [6] for a

review), in this paper we focused our attention on their structural properties. In fact even if their chemical composition is, obviously, strictly dependent on the target composition, their structure can be very different from both the target one and that of the sample homogeneous phase. Furthermore such a structural study is even more interesting when binary alloys are concerned. The presence of more than one chemical species gives rise to a variety of structural arrangements, which can be made more favorable if the appropriate deposition parameters are chosen. In the case of silicon carbon alloy the structural arrangements are in some way more complicated by the fact that carbon atoms can be found both in the sp^2- and sp^3-hybridized forms. The mechanical and optical properties of these silicon carbon alloys strongly depend on both the stoichiometry and on the sp^2/sp^3 carbon configuration ratio.

The investigation procedure was as follows: firstly we identify an area on the sample surface which can be considered representative of the overall surface topology of the sample. Then Raman spectra were collected over such an area. An analysis of the Raman spectra allowed the detection of four different structural typologies as shown in Fig. 2, and labeled as (a), (b), (c) and (d). Finally, four maps were obtained by reporting the values of the integrated area of a Raman band, typical of each of the identified typologies. As can be seen from Fig. 2 the Raman spectra look very different as a function of the sampling point, reflecting different local structural arrangements. Raman spectrum (a) is characterized by a strong feature typical of crystalline silicon, the position of this line is red-shifted with respect to its natural position in the infinite silicon lattice, indicating the presence of a microcrystalline silicon phase. The presence of amorphous silicon is indicated by the asymmetrical shape of the line showing a tail towards the low energy side. Weaker features at 900 cm^{-1} and in the 1300–1500 cm^{-1} are due to second order crystalline silicon and amorphous carbon. There is no evidence of the presence of SiC bond Raman scattering features. Silicon related structures in spectrum (b) are similar to the above reported ones. The strongest differences are evident in the region where the C—C bond Raman contributions are expected. Two sharp Raman lines are superimposed to a rather broad and weaker band. The more intense of these lines is located at 1579 cm^{-1} and is ascribed to the E$_{2g}$ stretching mode of C—C in graphite. There is also an evident shoulder at 1620 cm^{-1} [7]. The second line, located at 1334 cm^{-1}, has been attributed to the presence of very small crystallites of graphite [8,9], in such a case it should be due to the A$_{1g}$ mode of C—C in graphite, which is Raman inactive. Such a mode becomes Raman active and its intensity is proportional to the inverse of the graphite crystallite size as a consequence of the breakdown of the κ selection rule in a system with no long range order. Spectrum (c) is typical for fully amorphous material. The following spectral features are evident: a band at 480 cm^{-1} which arises from amorphous silicon; a more intense, peaked at 1410 cm^{-1}, is due to sp^2 amorphous carbon, with a
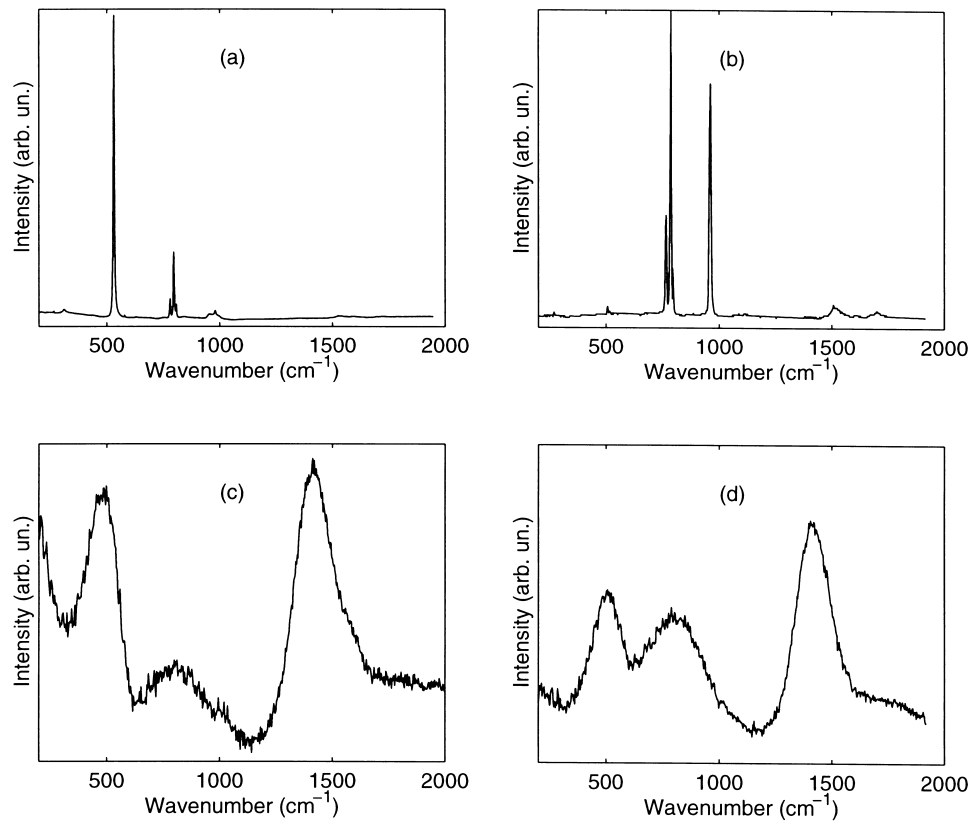
Fig. 4. Raman spectra of the two targets (a) reaction bonded SiC and (b) 6H-SiC; (c) and (d) are the corresponding Raman spectra of the homogeneously distributed phase of the films.

shoulder at 1600 cm^{-1} originating from the presence of graphitic islands; a relatively strong and broad band peaked around at 800 cm^{-1} is typical for amorphous SiC configuration. No evidence of the 1334 cm^{-1} line is observable. Spectrum (d) is similar to the latter one but it seems related to a more carbon rich phase as evidenced by the lower intensities of both the amorphous silicon and SiC bands. Such a findings seems confirmed by the larger graphitic contribution to the C—C band at 1590 cm^{-1}. Even in this case the microcrystalline graphite band, expected at 1334 cm^{-1}, is absent.

In Fig. 3 we have reported the values of the integrated area for a characteristic Raman band of each spectrum. In particular we chose for spectrum (a) the area of the c-Si TO peak, for spectrum (b) the area of the peak E$_{2g}$ of graphite, for spectrum (c) the area of the a-Si TO peak (integration was performed on a frequency range chosen in such a way as to exclude contributions from the crystalline peak), for spectrum (d) the amorphous carbon band. As can be seen from the images, the crystalline contributions of silicon and graphitic carbon are localized mainly in the micrometer sized inhomogeneity present in the investigated area, which can be identified with the brightest area near the center of Fig. 3a,b. The homogeneously distributed phase is mainly amorphous in nature as evidenced by the almost uniform intensity distributions of the corresponding Raman

bands. Taking into account that the SiC Raman efficiency is lower than that of the C—C bond one,[10] and that SiC related Raman bands in a-SiC films could not be detected in a-SiC:H films [11], we expect that the density of such bonds in the homogeneous phase of our films should be relatively high.

In order to investigate the influence of the target material stoichiometry and structure we have grown, under the same experimental conditions some samples by using 6H-SiC polytype targets (even if we kept fixed all the deposition parameters, we expect some differences to occur owing to the high transparency of the 6H-SiC at the laser wavelength used). For comparison in Fig. 4a is reported the Raman spectrum of the reaction bonded SiC target. The main features of this spectrum is the strong peak at 520 cm^{-1} due to the Si—Si transverse optical phonon mode, which evidences the presence of a silicon rich phase. Other features are due to carbon atoms: the triplet in the 700–1000 cm^{-1} range arises from Si—C bonds, while weak features approximately at 1500 cm^{-1} can be due to graphitic island or amorphous carbon, probably existing in the interstitial regions between microcrystalline SiC or Si rich zones, or to second order scattering features of SiC [12]. The Raman spectrum of the 6H-SiC target is shown in Fig. 4b and as expected, there is no evidence of Si—Si phonon mode. SEM surface images of samples grown by using

this latter SiC target are similar to the one reported in Fig. 1, even if the inhomogeneity number density seems to be lower. In Fig. 4c,d we report the typical Raman spectrum of the homogeneously distributed phase of the two corresponding films. As can be seen, from a structural point of view, the two spectra are very similar and characterized by a well defined amorphous SiC band, beside the amorphous silicon and carbon contributions. The relative intensity of the a-Si band with respect the a-SiC one appears to be weaker in the sample grown by ablating the 6H-SiC target, but relevant structural differences between the two samples cannot be envisaged from the two spectra.

4. Conclusion

Films of a-SiC have been obtained by means of the PLA deposition technique. Structural investigation of the samples, by means of micro-Raman spectroscopy revealed a variety of structural arrangements. In particular some inhomogeneities, detected by SEM imaging, revealed silicon and sp^2 carbon microcrystalline structures, while the almost homogeneously distributed phase was revealed to be amorphous with an high Si—C bond density. Moreover, to investigate the influence of the target on the structure of the films, two different SiC targets were used: a polycrystalline reaction bonded SiC and a 6H-SiC polytype. The measured Raman spectra looked very similar to each other, suggesting the hypothesis that, under the deposition conditions adopted, the target structure had weak or no influence on the structure of samples. Even when micrometer or submicrometer sized particles, ejected from the target, are included in the film, their measured Raman spectra appeared different from the target ones. It seems that these very energetic particles relax structurally on the sample surface producing a segregation of silicon and carbon atoms. The structure of these segregated phases can range from the amorphous to microcrystalline. As an example we observed the presence of microcrystalline graphite, otherwise absent in the target. Due to both its high spatial resolution and the ability to collect a large number of spectra over properly selected areas, Raman microscopy revealed itself to be an excellent and reliable tool in the investigation of the properties of complex structural systems such as PLA deposited films.

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