

Raman spectroscopy, a new facility at LECI laboratory to investigate neutron damage in irradiated materials.

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Abstract : Raman spectroscopy is considered as a good alternative to X-ray diffraction analysis in order to study the irradiation damage in materials. Up to now LECI hot laboratory had only an X-ray diffractometer in hot cell to characterize the evolution of the crystallographic structure of materials under irradiation. The present paper describes a new Raman spectroscopy facility available in the “M line” of LECI laboratory. This new facility consists in a T64000 Jobin Yvon spectrometer associated with an Ar laser ($\lambda = 514 \text{ nm}$) and two microscopes. The first one is located close to the spectrometer and the Ar laser, and is dedicated to studies of non irradiated materials. The second microscope takes place in a hot cell in order to characterize irradiated samples and is linked to the Ar laser and the spectrometer thanks to optical fibres. The main advantage of such a facility in comparison with X-ray diffraction is the opportunity of performing very local investigations. Indeed, it is possible to focus the laser on $1 \mu\text{m}^2$ for a bulk resolution of few μm^3 . Today, this new facility is totally operational and studies have already been performed: For instance, evolution of the microstructure of ions irradiated SiC singlecrystals, or local investigations in zirconia layers of PWR claddings.

KEYWORDS : Raman spectroscopy, microstructure, local analysis, irradiation damage.

1. INTRODUCTION

The extension and the refurbishment of the LECI laboratory in Saclay began about ten years ago and are now completed. The authorization to begin studies on radioactive samples in the new facility called “M line” was given in October 2005 by the French Nuclear Safety Agency. Before this refurbishment, the only way to obtain crystalline / crystallographic informations on irradiated samples in LECI laboratory was the X-ray diffraction. If this experimental method is very interesting, it needs macroscopic samples and is not able to perform very local investigations. Indeed the typical area analysed with the X-ray diffractometer of LECI laboratory is about 0.5 cm^2 . In order to perform crystalline analysis on irradiated samples at a local scale (few μm^2), a Raman facility was developed in the “M line” with the particularity to allow Raman acquisitions with irradiated and non-irradiated samples. Such studies are possible thanks to two analysis stations, one located in a shielded cell, the other in a room close to the cell.

2. EXPERIMENTAL APPARATUS

2.1 DESCRIPTION OF “M LINE” OF LECI LABORATORY

The new “M line” of LECI laboratory is composed of 19 shielded cells in lead with inner stainless steel casing. The two main interests of these casings are an excellent containment of radioactive contamination and easier dismantling operations when it will be necessary. A global view of M line is given in figure 1. “M line” is composed of two cells lines, “east line” and “west line”. Most of the 19 shielded cells are dedicated to mechanical studies. Two cells are storage ones (M08 and M15) and three others are devoted to samples preparations for microstructure analysis (TEM and EMPA) and Raman acquisitions. The Raman microscope is located in the M16 cell.

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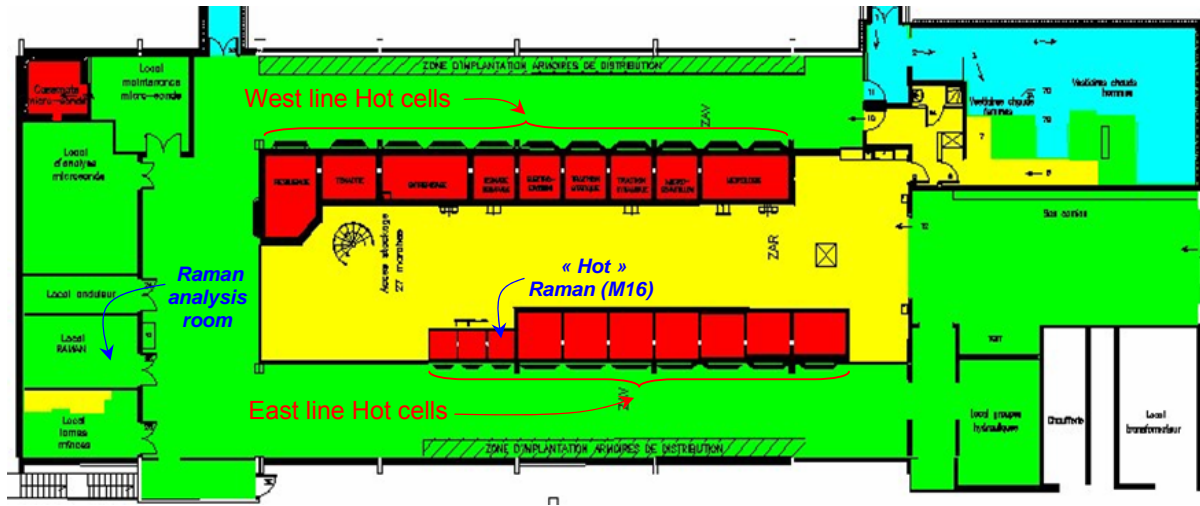


Figure 1: "M line" of LECI laboratory.

2.2 DESCRIPTION OF RAMAN SPECTROMETER

The Raman facility of LECI laboratory is composed by a T64000 Jobin Yvon spectrometer with a double subtractive stage, a Spectra Physics Ar laser ($\lambda = 514 \text{ nm}$) and two Olympus microscopes (BX40 and BX50) with magnifications of X10, X50 and X100. The laser can reach a 4 W maximum power and an X-Y motorized plate is available on the two microscopes. The general characteristics of this equipment are a lateral resolution of 1 to 2 μm^2 , a z resolution of 1 μm and an analysed volume of few μm^3 for opaque samples (for transparent samples, this analysed volume can reach few hundred μm^3). As mentioned previously, this facility is able to perform acquisitions for irradiated and non irradiated samples. The laser, the spectrometer, and the first microscope (BX40) are located in a room (analysis room) quite close to the "east line hot cells" where it is possible to study non irradiated samples (figure 2). For the study of irradiated samples, a second microscope (BX50) is located in the M16 shielded cell. This microscope is linked to the laser and the spectrometer thanks to two optical fibres. First one brings the laser beam to the irradiated samples and the second collects the Raman signal and brings it to the spectrometer for analysis (figure 3). Thanks to a selection mirror, it is possible to send the laser beam on the BX40 microscope for the study of non irradiated samples, or to send it to the BX50 microscope through the optical fibre for Raman acquisition on irradiated specimens.

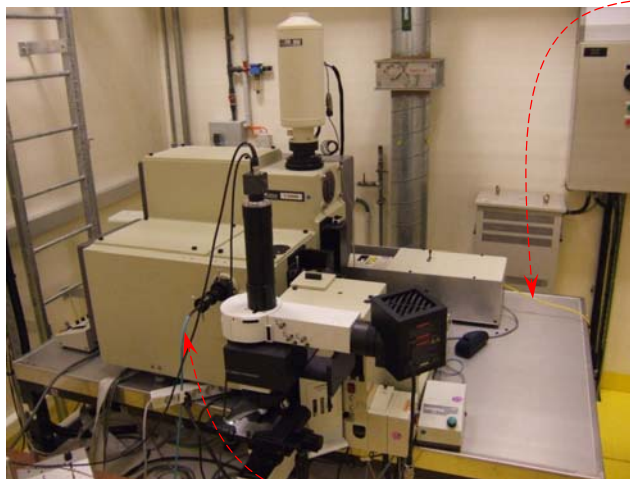


Figure 2: Raman analysis room.

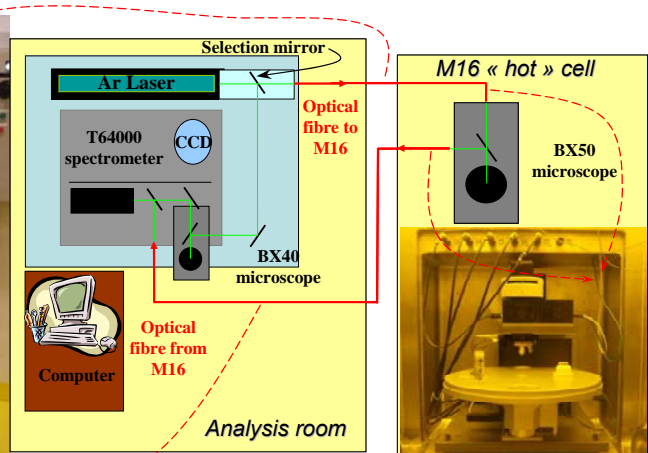


Figure 3: "Hot" and "cold" part of the Raman facility.

Another characteristic of the Raman facility for non irradiated samples is the possibility to perform confocal measurements. Previously it was mentioned that the typical analysed volume for a sample is about few μm^3 . In the case of transparent samples, this volume is much bigger because the laser can go through the entire sample and the Raman diffusion can come from the entire sample too. In the aim to improve the bulk resolution for such samples, it is possible (thanks to conjugated pinhole diaphragms) to select a small part of the Raman diffusion of the sample, just close to the focus point chosen for the laser (figure 4). All the Raman diffusions coming from a given distance above or below the focal point of the laser are not able to pass through the pinhole and so do not contribute to the Raman spectra. The main interest of this device is to be able to perform Raman acquisitions at different deep within the sample without any mechanical operations (polishing, etching...) with a high z resolution.

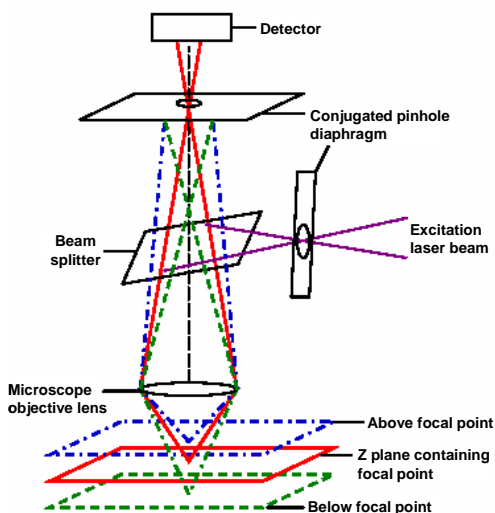


Figure 4: Description of confocal system.

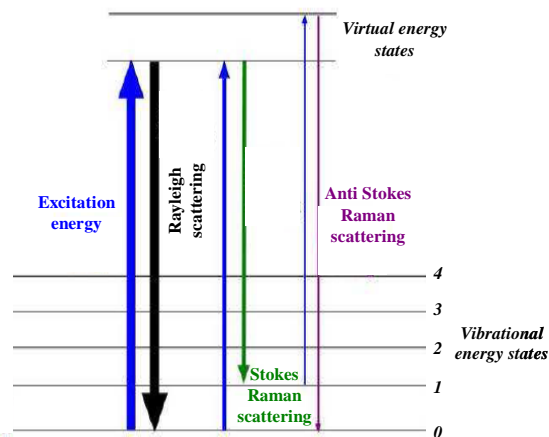


Figure 5: Energy level diagram showing the states involved in Raman.

3. EXAMPLES OF EXPERIMENTAL RESULTS

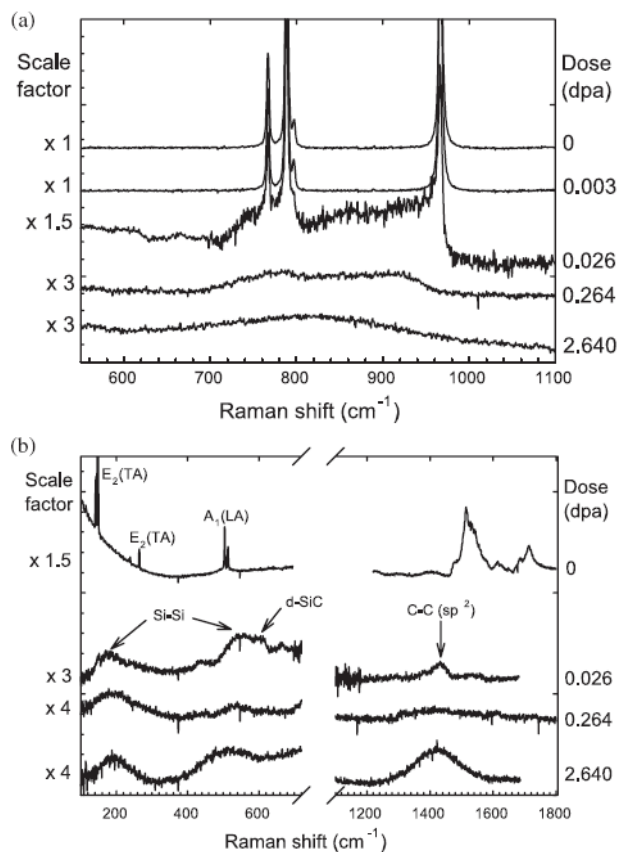
3.1 RAMAN THEORY

Raman spectroscopy is based on the detection of the vibration modes of molecules and crystals, which allows chemical identifications and determinations of the crystalline structure of a sample. It consists in the characterisation of the material using the inelastic scattering, or Raman scattering, of a monochromatic light near the visible range of wavelength. The incident photon excites one of the vibration energy level of a molecular bond of the sample, which is released to a higher energy state. The vibration state of the molecular bond then decreases to its initial energy or another energy level close to its initial one. During this luminescence, a photon is emitted. The wavelength of this photon is a signature of the material (figure 5). Raman spectrometry can then characterises a material, each band of the spectrum being characteristic of a type of bond in the vibration mode of the molecule / crystal analysed. This experimental technique is non destructive, do not need any preparation of the samples and has the advantage to allow very local characterizations (that it is not the case for X ray diffraction). In the other hand, Raman spectroscopy gives only qualitative results and, for instance, do not allow quantifications of different phases in a sample.

3.2 EXAMPLE OF STUDY ON IONS IRRADIATED SAMPLES [1]

This fundamental study was led in the framework of silicon carbide behaviour under irradiation, this material being proposed for structural components in harsh environment such as nuclear reactor of 4th generation. Raman spectroscopy was used to investigate the structure of 6H α -SiC single crystals irradiated at room temperature with 4 MeV Au ions. The fluences were varied from 10^{12} to 10^{16} cm^{-2} and the beam current density was maintained in the range of 0.1 – 2 $\mu\text{A cm}^{-2}$ to avoid high-dose-rate effects and excessive target heating. Raman scattering and confocal Raman spectra were recorded at room temperature. The laser intensity was kept around 30 mW to avoid any heating of the sample. To analyse the different Si–Si, Si–C and C–C related modes, the spectra were measured in the broad spectral range between 15 and 1800 cm^{-1} . Raman spectra of Au-irradiated α -SiC at room

temperature are shown in figures 6(a) and (b). Their evolution is significant of a modification of the local structure induced by irradiations. For the lowest dose (0.003 dpa), the irradiated sample spectrum is similar to the virgin one, which suggests that α -SiC is weakly damaged or is undamaged. At moderate dose (0.026 dpa), three broad bands appear around 200, 520 and 1420 cm^{-1} in addition to the first-order lines of crystalline SiC. They are characteristic [2] of Si-Si (200 and 520 cm^{-1}) and C-C homonuclear bonds (1420 cm^{-1}).



Figures 6: Raman spectra of Au-ion irradiated 6H-SiC at room temperature: (a) first-order and (b) second-order peaks. Figures from [1].

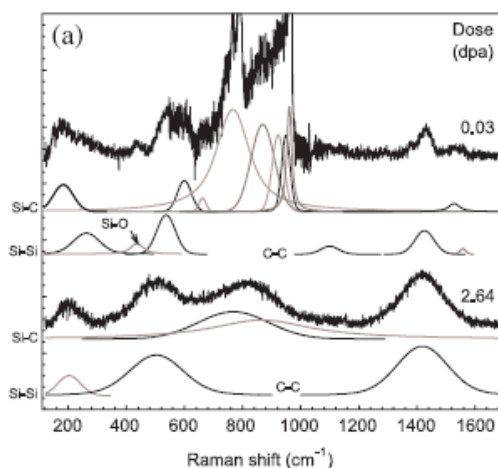


Figure 7: Curve fit and spectrum for a sample irradiated with Au ions at RT for 0.03 dpa and 2.64 dpa. Figure from [1].

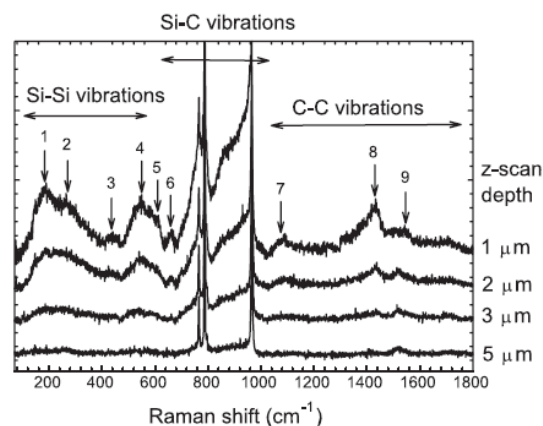


Figure 8: Confocal Raman spectra for different z-scan depths of RT Au-ion-irradiated α -SiC for 0.026 dpa. Figure from [1].

More than 20 bands were necessary to fit the Raman spectrum recorded for a sample irradiated at 0.026 dpa (figure 7). They are associated with the vibrations of silicon (20– 600 cm^{-1}), silicon carbide (700–1000 cm^{-1}) and carbon (1100–1800 cm^{-1}). Figure 8 shows corresponding confocal spectra recorded for the same sample at various z-scan depths. For the $z = 1 \mu\text{m}$ scan, the Raman spectrum is composed of nine bands in addition to the characteristic crystalline peaks of SiC. Their intensities decrease when the z-scan depth increases. Simultaneously, the four crystalline peaks become sharper. For a depth scan of 5 μm , the Raman spectrum is similar to that of the virgin sample. Obviously, the nine bands are related to the damaged layer and the crystal line peaks are issued from the non-irradiated part of the sample. In fact the Raman spectrum of irradiated SiC is composed of two contributions from the irradiated layer and the non-irradiated part of the sample because SiC is transparent to the laser light [2, 3]. It is also possible to identify the band around 1520 cm^{-1} as the second-order Raman lines of crystalline SiC. The increase of the dose induces a decrease of the crystalline peak intensity and an enhancement of homonuclear band intensity (figures 6(a) and (b)). The crystalline peaks completely vanish for

2.64 dpa, probably because of the increased absorption of the Ramanscattered light by the damaged layer. The crystalline peaks are not directly observed in the spectrum of the sample irradiated at 0.264 dpa, but simulation of the corresponding Raman spectrum showed that these bands are still necessary to the fit. For the highest dose (2.64 dpa), only four broad bands remain at wavenumbers around 200, 500, 800 and 1420 cm^{-1} . The corresponding fitted spectrum is reported in figure 7. Only five bands are necessary to reproduce the Raman spectrum, equally distributed over the three domains of vibrations Si–Si, Si–C and C–C. The fit also puts in evidence a broadening of the bands upon irradiation. This is probably due to the amorphization of the irradiated layer. The structural evolution is in agreement with previous studies on irradiated SiC [3,4]. Indeed, the Raman spectrum of irradiated SiC generally presents several bands in the Si–Si, Si–C and C–C vibration domains and a clear decrease of the Raman line intensities (figures 6(a) and (b) and 3). The principal effect shown by Raman spectroscopy is the formation of homonuclear bonds. However, the process is still not elucidated. For Si–Si bonds, it might consist in the replacement of the carbon atom, kicked out by the ion used for irradiation, by a silicon atom and vice versa. For the formation of C–C bonds, the proposed mechanism is based on the accumulation of interstitials or antisite carbon via condensation of C interstitials generated on the path of ions [5,6].

3.3 EXAMPLE OF STUDY ON NEUTRON IRRADIATED SAMPLES

This study was performed in the framework of the oxidation behaviour of zirconium alloy under irradiation. The aim of this study was to detect and compare the relative content of two crystalline phases of zirconia within the oxide layer of a zirconium alloy sample in order to try to locate an eventual concentration of one of the phases at the metal / oxide interface. This sample has a 5 μm thick zirconia layer and was cut in radial direction to allow Raman acquisitions at the external surface of the zirconia layer and close to the metal / oxide interface (figure 9). Because of the quite important absorption of the laser intensity by the optical fibres, acquisitions were performed with a laser power set at 1.6 W. Spectra, recorded between 14 and 1300 cm^{-1} for an acquisition time of 300 seconds, are given in figure 10.

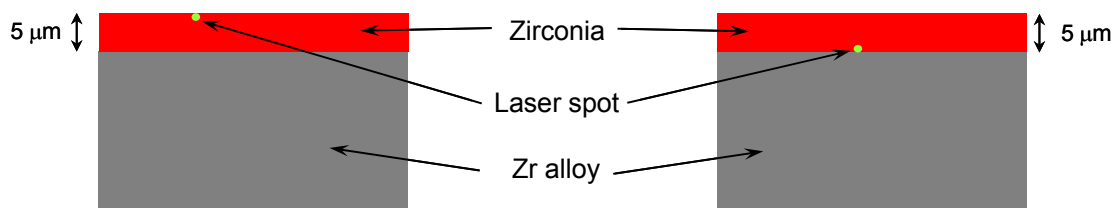


Figure 9: Localisation of the laser spot for the acquisitions performed near the external surface and the metal/oxide interface of the zirconia layer.

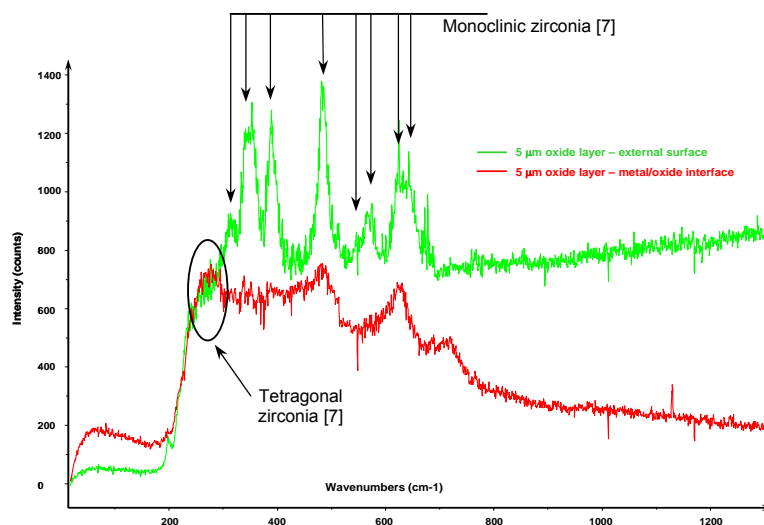


Figure 10: Raman spectra acquired on the irradiated sample at the external surface of the zirconia layer and at the metal / oxide interface.

A qualitative comparison of the intensity ratio of Raman bands associated to monoclinic and tetragonal zirconia has been performed for the two acquisitions. The intensity of Raman bands were estimated after a curve fitting of the different spectra with Labspec software. For each phases, the selected bands used to calculate these ratios were the more important ones. For tetragonal zirconia, two bands were selected, those located at 265 cm^{-1} and 455 cm^{-1} . For monoclinic zirconia, four bands were selected, respectively located at 338 cm^{-1} , 351 cm^{-1} , 388 cm^{-1} and 483 cm^{-1} . Results are given in table 1. It is important to specify that these ratios do not allow any quantification of the tetragonal or the monoclinic phases in the oxide layer. The characterizations performed at the external surface of the oxide layer show that monoclinic zirconia is widely present (tetragonal phase is difficult to observe directly on the spectra without fitting). In the other hand, the spectra performed at the metal / oxide interface clearly exhibits an important enrichment of tetragonal phase. This is clearly shown by the results of table 1, but also by the spectra of figure 10 where one can see the arising of an important band located at 270 cm^{-1} .

Irradiated sample with a 5 μm oxide layer		
Analysed area	External surface	Metal / oxide interface
R (T / M)	0,11	0,83

Table 1: Qualitative comparison of Raman intensity bands for tetragonal and monoclinic zirconia.

4. CONCLUSION

A Raman spectroscopy facility, allowing acquisitions on non irradiated and irradiated samples, was recently developed in Saclay during the refurbishment of the LECI laboratory. This facility is composed by a T64000 Jobin Yvon spectrometer with a double subtractive stage, a Spectra Physics Ar laser ($\lambda = 514\text{ nm}$), two Olympus microscopes (BX40 and BX50) with magnifications of X10, X50 and X100 and a confocal system which gives for the confocal Raman microprobe the ability to discriminate between parts of the sample that are not at the same depth (optical sectioning). The laser, the spectrometer with the confocal system, and the first microscope (BX40) are located in an analysis room where it is possible to study non irradiated samples. For the study of irradiated samples, a second microscope (BX50) is located in the M16 shielded cell and is linked to the laser and the spectrometer thanks to two optical fibres. The Raman facility is operational since October 2005 in "M line" of LECI and several studies have been decisively performed with non irradiated and irradiated samples. In future, in order to improve the accuracy of detection and also to allow easier acquisitions, it is foreseen to replace the old acquisition system for a newer one. This restoration could be achieved during 2008.

- [1] S. Sorieul, J.M. Costantini, L. Gosmain, L. Thomé and J.J. Grob, "Raman spectroscopy study of heavy-ion-irradiated α -SiC", *J. Phys.: Condens. Matter* **18** (2006) 5235–5251.
- [2] H. Hobert, H. Dunken, R. Menzel, T. Bachmann and W. Wesch, *J. Non-Cryst. Solids* **220** (1997) 187–194.
- [3] W. Bolse, J. Conrad, T. Rödle and T. Weber, *Surf. Coat. Technol.* **74/75** (1995) 927–931.
- [4] W. Bolse, *Nucl. Instrum. Methods Phys. Res. B* **141** (1998)133–139.
- [5] L.A. Rahn, P.J. Colwell and W.J. Choyke, *Proc. 3rd Int. Conf. on Light Scattering in Solids* ed. M Balkanski, R C C Leite and S P S Porto (Paris: Flammarion) (1976) p 607.
- [6] A. Mattausch, M. Bockstedte and O. Pankratov, *Phys. Rev. B* **70** (2004) 235211.
- [7] P. Barberis, T. Merle-Méjean, P. Quintard, *J. Nucl. Mat.* **246** (1997) 232-243.