CVD diamond wires and tips for x-ray detection: growth and characterisation by SEM and micro-Raman spectroscopy

C. Manfredotti*, F. Fizzotti*, A. Lo Giudice*, G. Mucera*, P. Polesello*, E. Vittone*, G. Mariotto#, C. Vinegoni#, E. Cazzanelli@

* Università di Torino, Dipartimento di Fisica Sperimentale, INFN-Sezione di Torino, INFM-Unita' di Torino Università, Via P. Giuria 1, I-10125 Torino, Italy
# Università di Trento, Dipartimento di Fisica, INFM-Unità di Trento, Via Sommarive 14, I-38050 Povo (TN), Italy
@ Università della Calabria, Dipartimento di Fisica, I-87036 Arcavacata di Rende, Italy

ABSTRACT

We present a systematic study of the growth of polycrystalline diamond thin films on W wires (50-500 μm diameter) and tips by hot filament assisted chemical vapour deposition (HFCVD) for x-ray detection purposes. We carry out correlations between Scanning Electron Microscopy (SEM) observations and micro-Raman (μ-R) spectra, while varying different growth parameters (wire and tip diameter, CH_4/H_2 ratio, working pressure). SEM observations show a uniform covering of the substrate, with growth rates ranging from 0.5 to 1.5 μm/h. All μ-R spectra show a well defined diamond peak at 1330.8-1333.7 cm^{-1} together with a broad structure at 1400-1600 cm^{-1} and a luminescence background extending over the whole scanned range (500-2000 cm^{-1}). A close analysis shows that best quality is obtained with the lowest diameter substrates, at the lowest CH_4 concentration and at a low pressure. Some depositions have been studied as x-ray detectors and their sensitivity at low energy and 6 MeV beam evaluated, showing a good response with respect to standard ionisation chambers.

Keywords: diamond thin films, HFCVD, Scanning Electron Microscopy, micro-Raman spectroscopy, x-ray detectors

1. INTRODUCTION

Among its excellent properties, diamond has some which make it attractive for radiation (UV, x-ray, nuclear radiation) detection purposes. It has, in fact, a very high resistivity, a very large saturation velocity, a very high radiation hardness and chemical inertness, and it is a also tissue equivalent material (Z = 6 against Z = 6.7 for biological tissue), which makes it very interesting in the field of dosimetry[1,2,3]. In the last decade, low pressure Chemical Vapour Deposition (CVD) methods have allowed the synthesis of polycrystalline films with electronic quality comparable to natural samples, so that we can actually speak of "detector grade" CVD films[4]. Among the different CVD growth processes, Hot Filament CVD has the advantage of being a low price and easy to set up technique, which allows diamond films to be grown also on different geometries from planar, such as cylindrical or needle-like[5]. It should be possible to obtain by this way position sensitive detectors suitable for in-vivo measurements with a response directly proportional to the absorbed dose.

Several studies report the relationships between growth parameters and diamond film properties, showing their strict dependence on features such as film thickness, crystallite size, diamond content, etc[6]. Among the several analytical techniques, Raman is the one which can give a good insight into the "diamond quality" of the film, because of its sensitivity to C bond type[7,8]. Besides, the possibility to use a microprobe for excitation allows to take spectra also on very small regions of the sample: it is therefore possible to characterise films grown on very small substrates, such as thin wires, with a better signal to noise ratio and the possibility to focus on well localized zones.

We present in this work a systematic study of the growth parameters in order to obtain diamond films on metallic wires and tips to be used as x-ray dosimeters. For this purpose, micro-Raman and SEM characterisation has been carried out, and some samples have been tested under x-ray beams irradiation[3].

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2. EXPERIMENTAL

Diamond films on tungsten wires and tips have been grown in a HFCVD apparatus described in a previous paper[9]. Two tantalum wires (0.25 mm diameter) are wound into helical shapes with about 2 mm turn diameter. The two hot filaments were heated up to 2300°C as measured by an optical pyrometer. The filaments were located 8 mm apart each other and at a 6 mm distance from the substrate which consists of tungsten wires and tips (50 mm long). Substrates with different diameters (ranging from 50 up to 500 μm) have been used. The two filament geometry ensures a good uniformity of deposition also for 0.5 mm diameter substrates. The temperature of the substrate wire was not directly measured because of the difficulty in placing a thermocouple through the wire. However a rough mapping of the temperature field close to the filament indicates a substrate temperature ranging from 900 to 1000°C[9]. A gas mixture consisting of H_2 at 750 sccm (standard cubic centimeters per minute) flow rate and CH_4 at a concentration ranging from 0.25% to 1% has been used. Working pressures varied from 5 to 80 mbar and wire diameters from 50 to 500 μm.

In order to test the quality of our films and correlate it with their growth parameters, SEM and micro-Raman spectroscopy analyses have been performed. Secondary electron images have been taken with a Leica 420 Stereoscan scanning electron microscope. In order to be used later for electrical characterisation, the samples have not been previously metallised, but analysed at low accelerating voltage (< 10 kV) in order to avoid charging phenomena. Raman scattering experiments were carried out using a microprobe set-up consisting of an Olympus microscope (model BHSM-L-2) coupled to a 1 meter focal length double-pass Jobin-Yvon monochromator (Ramanor, model HG2-S) equipped with holographic gratings (2000 lines/mm). The microscope objective (magnification 100X and numerical aperture NA= 0.95) served the dual role of focusing the incident radiation over a micrometer-sized region of sample (with a lateral resolution of about 1 μm) and of collecting the scattered light to be sent to the spectrometer for the analysis. The filtered radiation was detected by a cooled (-35 °C) photomultiplier tube (RCA, model C31034A-02) interfaced to a standard photon counting system. The signal was stored in a multichannel analyser and then sent to a microcomputer for the analysis. Spectra characterised by a good signal-to-noise ratio were recorded in the Stokes region between 500 and 2000 cm^{-1} from wires under excitation of the 488 nm line of an Ar^+ ion laser for irradiation densities of the order of $2x10^4$ Wcm^{-2}, in correspondence to which no photodegradation of the materials was observed.

After having established the parameters for a reproducible deposition of good quality films on tungsten tips, depositions have been carried out on tips made from 200-300 μm diameter wires. Films grown on 200-300 μm diameter wires and tips with a 0.5 % CH_4/H_2 ratio at 30 mbar pressure have then been used for current measurements under x-ray irradiation, in order to test their performances as x-ray detectors in a MIM structure. To this purpose, a 200 Å Ti/1000 Å Au electrode has been evaporated on the growth side and the samples annealed at 600 °C in nitrogen in order to get an ohmic contact. The current responses of the samples have been studied with a Keithley 617 electrometer under irradiation from either 50-250 keV or 6 MeV x-rays and results have been compared with the ones given by a mod. IC 10 from Wellhofer Dosimetrie ionisation chamber[3].

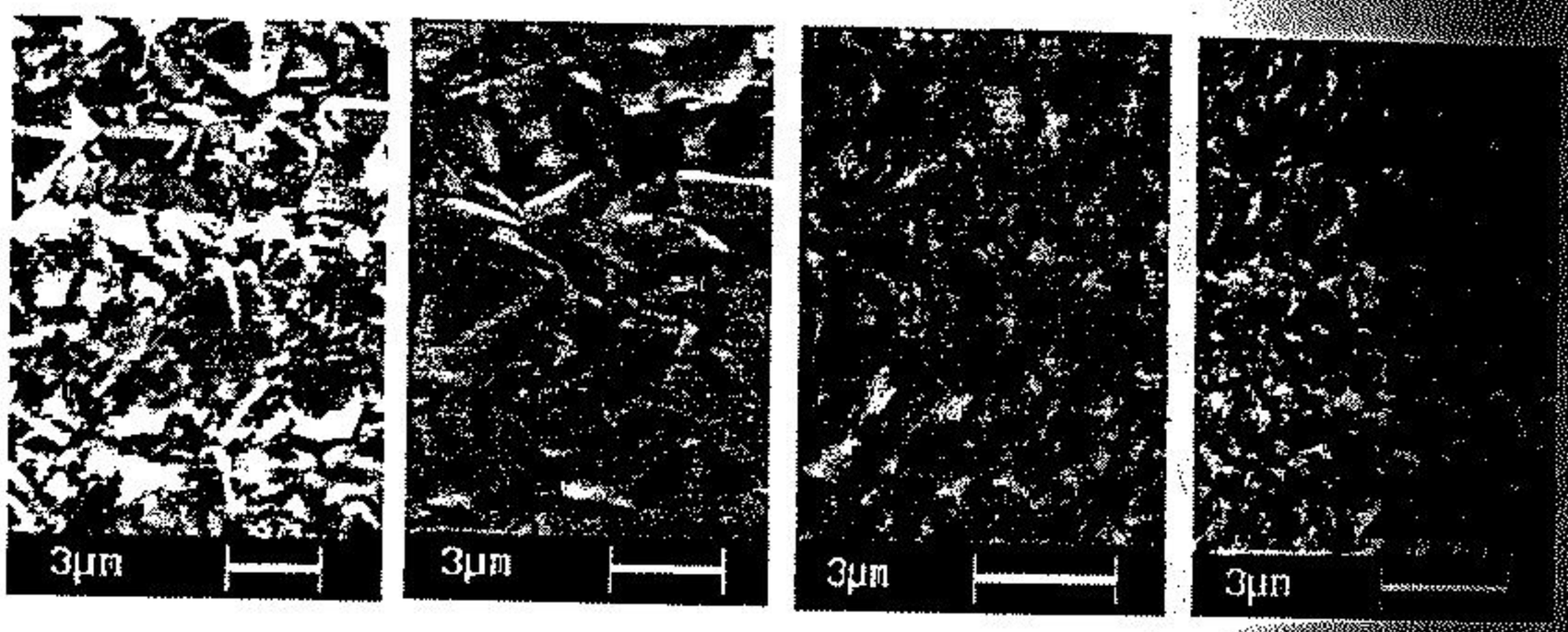
3. RESULTS AND DISCUSSION

Three series of depositions were studied, in which one deposition parameter (pressure, CH_4/H_2 ratio, wire diameter) was varied and the other ones kept constant. In Tab. I deposition parameters are reported. In every case, H_2 flows and distance from the hot filaments have been kept constant, and in every deposition tungsten substrate wires appeared completely covered by diamond films.

Fig. 1 shows SEM micrographs of several films grown under different conditions, in which different grain morphologies, from faceted to ballas type can be seen. From these micrographs, grain size and growth rate (defined as the ratio between film thickness and deposition time) can be estimated and compared with results obtained by an analysis of micro-Raman spectra. As pointed out by a two-dimensional model of a HFCVD reactor presented in Refs. 10,11, the cylindrical geometry should have a higher deposition rate than a planar one, due to the higher surface density and higher etching rate of hydrogen atoms and CH_x radicals over the substrate[10].

Tab. I: Deposition parameters of HFCVD films on W wires

Sample #	H_2 flow rate (sccm)	CH_4/H_2 ratio (%)	pressure (mbar)	wire diameter (μm)	deposition time (hrs)
1	750	0.33	80	300	6
2	750	0.33	15	300	6
3	750	0.33	5	300	6
4	750	0.33	30	300	6
5	750	0.33	60	300	6
6	750	0.5	30	300	6
7	750	0.75	30	300	6
8	750	0.25	30	300	6
9	750	1.00	30	300	6
10	750	0.5	30	300	6
11	750	0.5	30	200	6
12	750	0.5	30	100	6
13	750	0.5	30	50	6
14	750	0.5	30	500	6



(a) (b) (c) (d)

Fig. 1: SEM images of films grown on 300 μm W wires at p=30 mbar. CH_4/H_2 ratio: a) 0.25%, b) 0.5%, c) 0.75%, d) 1%.

Raman spectra of the samples are shown in Fig. 2 a), b), c): Raman intensities have been normalised over the value corresponding at the diamond peak, for comparison's sake. They all show a broad luminescence background, which extends over the whole scanned range, together with the characteristic narrow diamond peak at 1330.8-1333.7 cm^{-1} and the broad structure in the 1400-1600 cm^{-1} range to be ascribed to non-diamond features in the film (graphite or amorphous carbon)[7]. By a first visual comparison, we can see that the overall quality of the films is good; however, spectra corresponding to different deposition parameters look different.

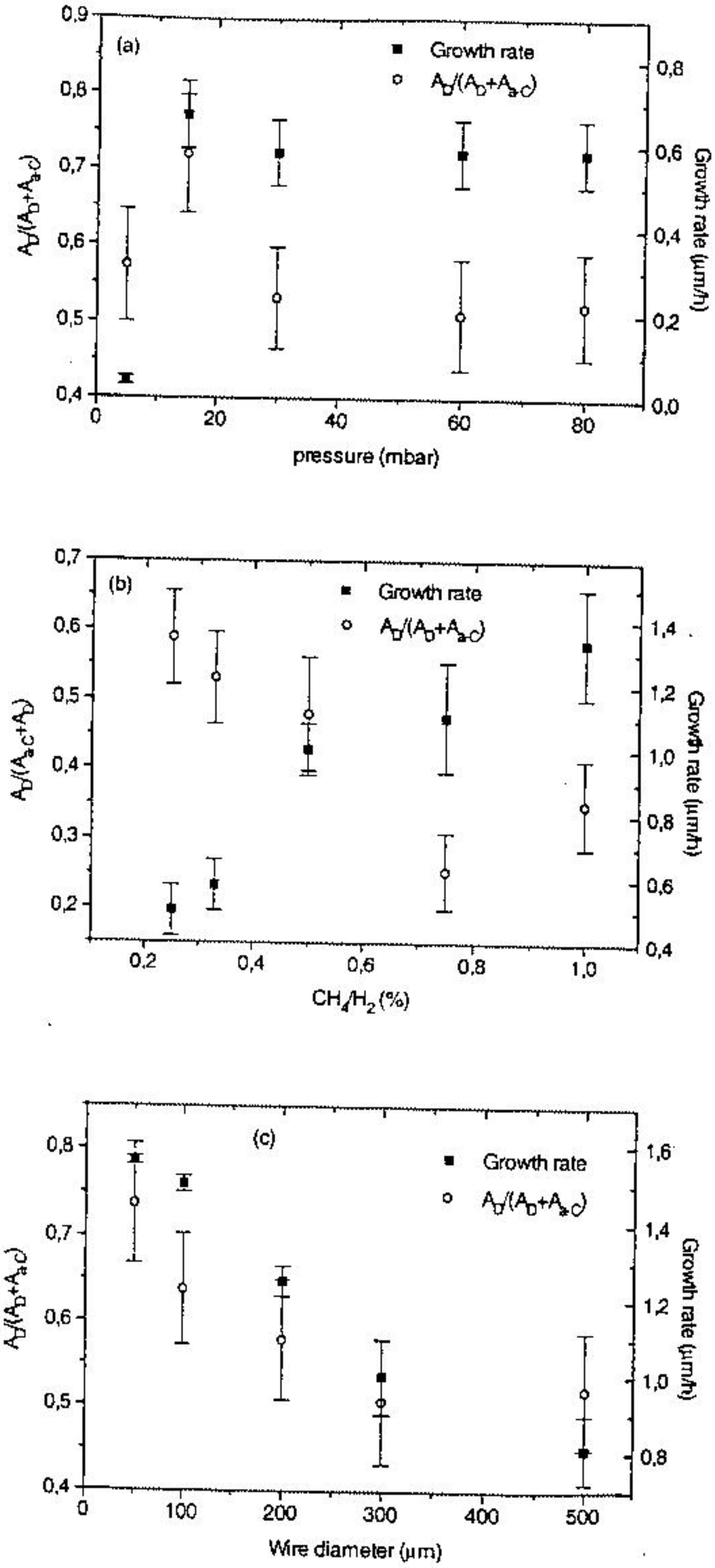


Fig.3: Area of diamond band/areas of diamond and non-diamond bands ratio and growth rate vs. variable deposition parameters. a): 0.33% CH_4/H_2, variable pressure, 300 μm diameter; b): p=30 mbar, variable CH_4/H_2 ratio, 300 μm diameter; c): 0.5% CH_4/H_2, p=30 mbar, variable diameter.

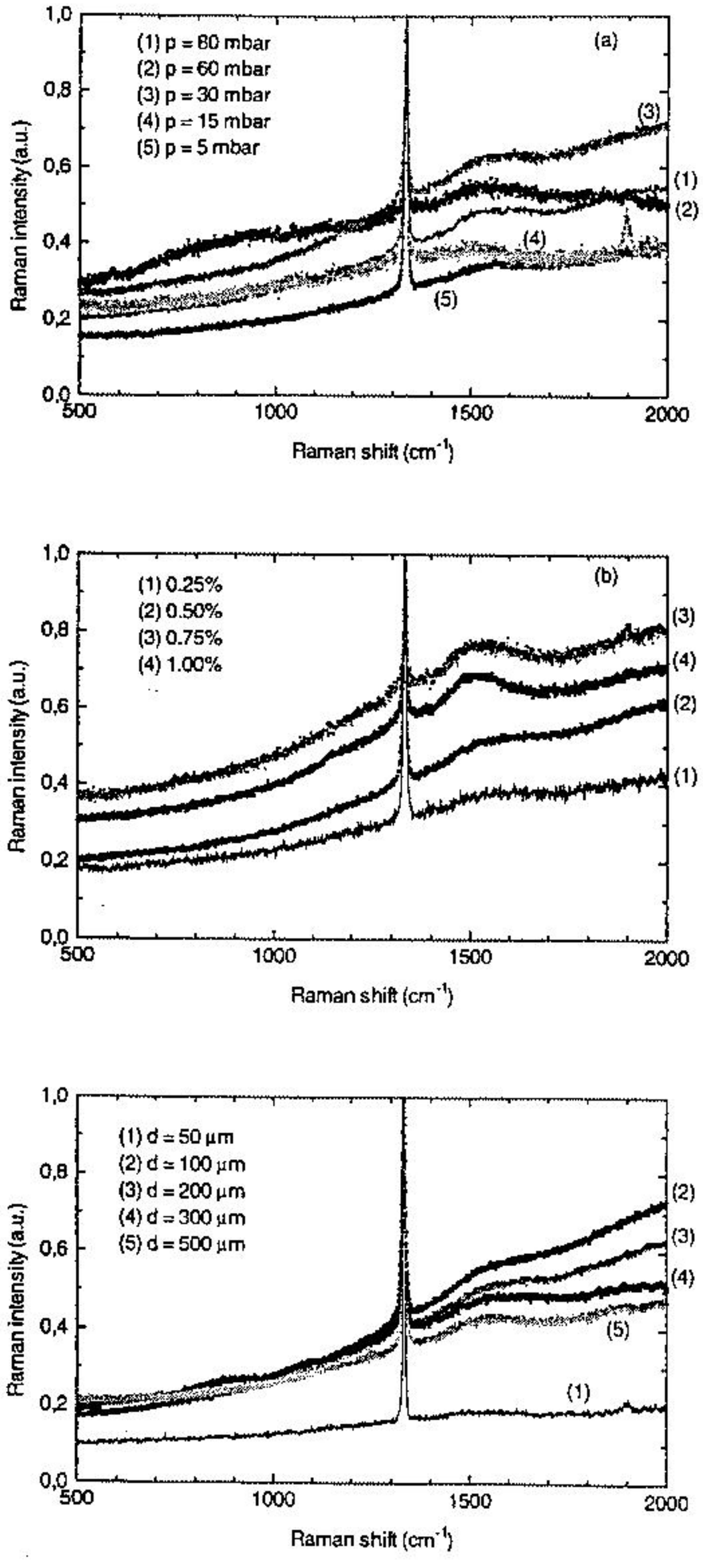


Fig. 2: µ-Raman spectra. Deposition parameters: a): 0.33% CH_4/H_2, variable pressure, 300 µm diameter; b): p=30 mbar, variable CH_4/H_2 ratio, 300 µm diameter; c): 0.5% CH_4/H_2, p=30 mbar, variable diameter.

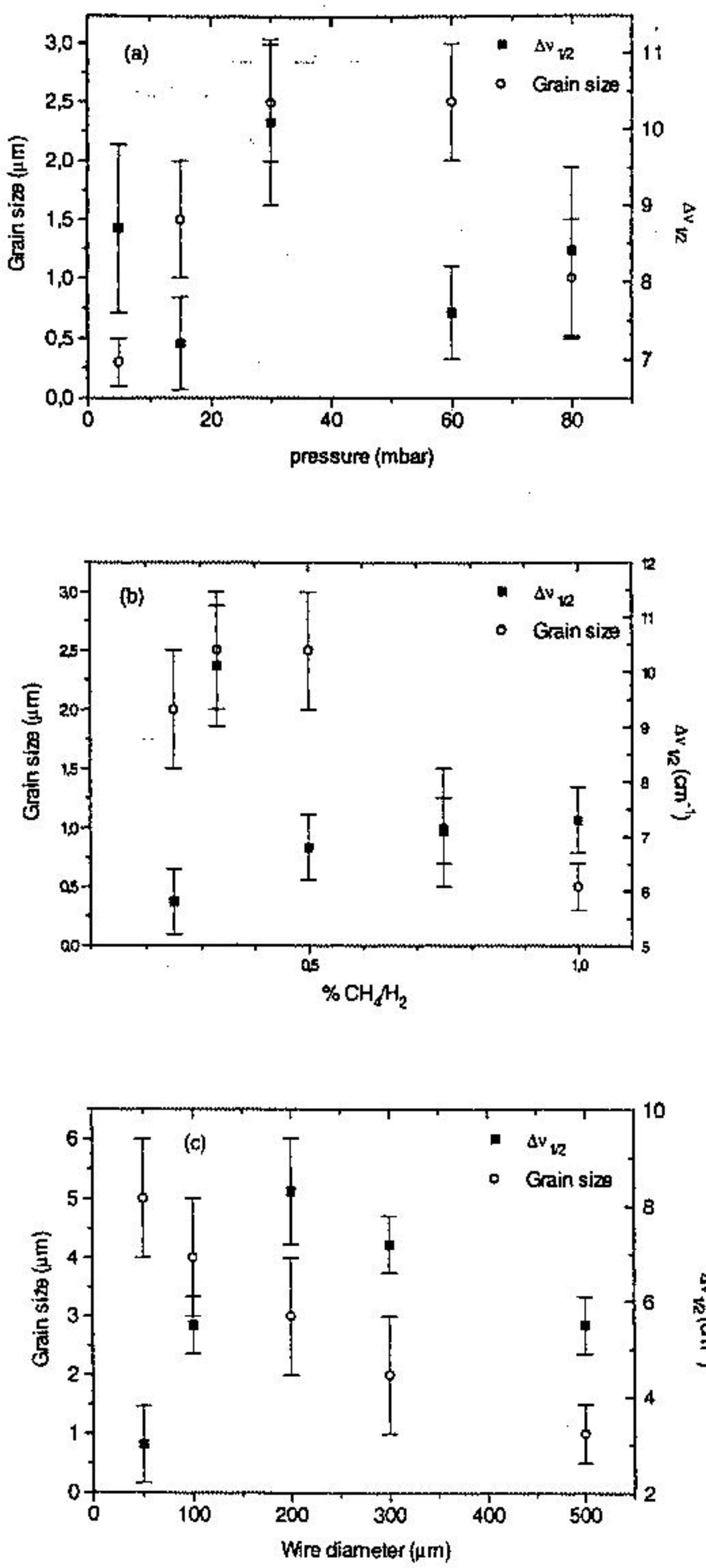


Fig. 4: Grain size and FWHM vs. variable deposition parameters. a): 0.33% CH_4/H_2, variable pressure, 300 μm diameter; b): p=30 mbar, variable CH_4/H_2 ratio, 300 μm diameter; c): 0.5% CH_4/H_2, p=30 mbar, variable diameter.

A closer analysis has considered two factors which are important in the study of diamond films: the ratio between the integrated intensity of the diamond peak and the integrated intensity of both the non-diamond and diamond structures ($A_D/(A_D+A_{a\text{-}C})$) and the full width at half maximum (FWHM) of the diamond peak. The former feature has to do with the relative diamond phase content of the film with respect to the non-diamond phase: it is not a direct measurement, as it depends on the different Raman scattering cross section for diamond with respect to graphite and on the different absorption coefficient at the excitation wavelength for the two materials[12]. However, an estimation of this ratio may be a good index of the "diamond quality" of the film which has to do with other properties, such as its electrical resistivity. The FWHM of diamond line is related to grain morphology and diamond domain dimension[8,13], as its deviation from the theoretical value estimated for natural diamond has to do with the spatial confinement of phonons in a microcrystalline structure[12,13]. This feature could be put into relation with the electrical properties of the films used as detectors, as they are greatly affected by defects and grain boundaries which act as recombination centres[4,15].

In Fig. 3 a), b), c), the ratio $A_D/(A_D+A_{a\text{-}C})$ and the growth rate (as estimated from measurements carried over SEM micrographs) are plotted against the parameters which have been varied (pressure in a), methane content in b), wire diameter in c)): areas have been calculated after having subtracted a linear background which kept into account as a first approximation the luminescence of the films. From these estimates we can have an idea of the best parameters for a good diamond film growth, which appear to be low pressure (about 15 mbar), low methane content and small wire diameter. However, a comparison of $A_D/(A_D+A_{a\text{-}C})$ values (ranging from 0.25 to 0.75) with the ones for growth rate (ranging from 0.5 to 1.5 μm/h) show a certain correlation, at least as regards films grown with a variation of pressure or wire diameter (Fig. 3 a), c)), whereas for films grown varying the methane concentration the trend looks opposite (Fig. 3 b)). The results for Fig. 3 a) and c) may thus be explained with the increase of diamond content with film thickness, confirming models presented in order to explain the relation of detector properties to film thickness[4]. The opposite result shown in Fig. 3 b) may have instead to do with the general lowering of crystal quality with the increasing of methane content, as confirmed by SEM observations[9].

In Fig. 4 a), b), c) the FWHM of the diamond peak and the grain size are plotted against the varying parameters (the same as in Fig. 3). In order to keep into account the instrumental slit width, linewidths have been corrected according to the graphical procedure described in Ref. 16, where the ratio between the experimental linewidth and the linewidth of a laser plasma line has been calculated and manipulated in order to deconvolute the real Lorentzian linewidth from the observed profile. Values for the corrected FWHM ranged from 3.0 cm^{-1} to 10.1 cm^{-1}, which is comparable with samples commercially available[14]. Differently from what we saw in Fig. 3, it is not easy to establish a correlation between these data and growth parameters and grain size as estimated by SEM micrographs[10]. Generally speaking, narrowest linewidths can be seen at low pressure, low methane content and small wire diameter, but the trend is not so clear, as there are some exceptions.

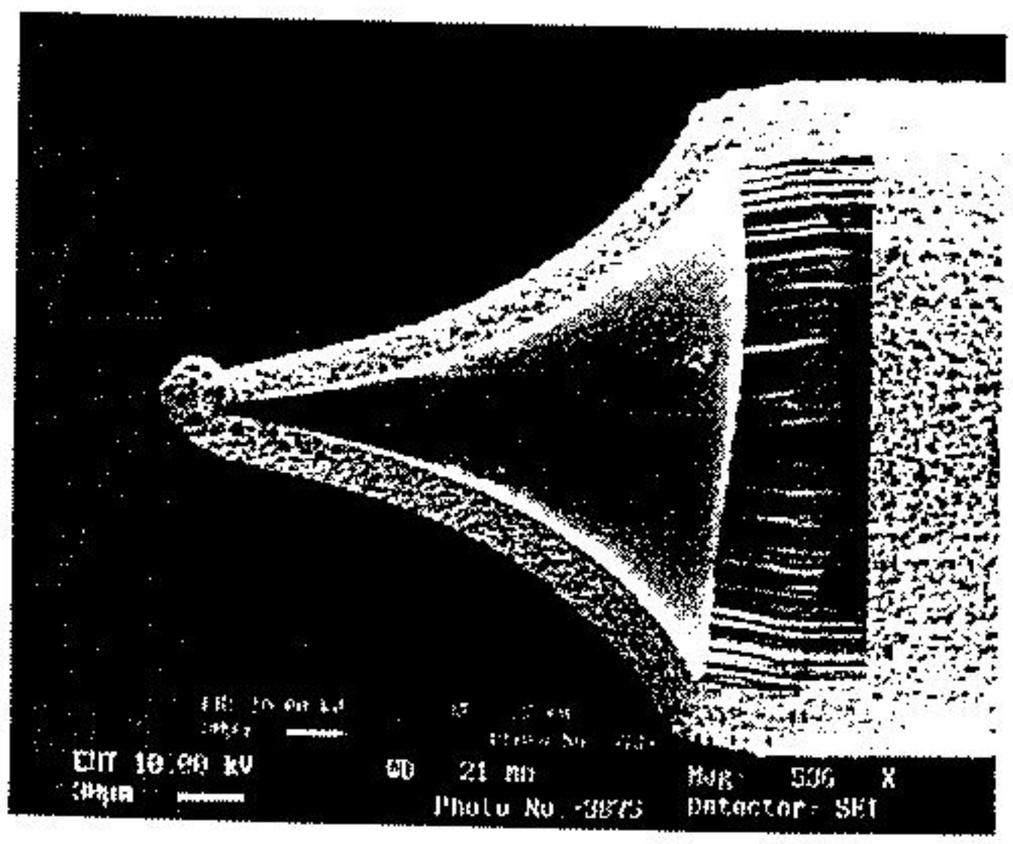


Fig. 5 Photomontage of a substrate tip over a CVD diamond film

By Raman analysis, also in a rough way, it is thus possible to establish the best deposition parameters in order to get films with good "diamond quality", and results confirm the SEM observations already reported in Ref. 10. However, in order to use diamond films for detecting purposes, other characteristics are required. Above all, an easy handling of the device and a film thickness not lower than 10 μm in order to have a sufficiently high electrical volume resistance are required: that rules out depositions on too small wires which could be easily broken or with too low methane concentration, which causes a too low growth rate. For this reason, a compromise between best material quality and best manageability is needed, also for the growth on tips. Fig. 5 shows a SEM micrograph of a diamond film grown over a sharp tip obtained from a 300 μm diameter tungsten wire. The picture is a photomontage where the picture of the substrate is superimposed over the photo of the deposition, thus showing the uniformity of the deposited film and giving an estimate of its thickness, which turns out to be ~ 15 μm. In Fig. 6 the I-V characteristics of a diamond tip in dark (squares), under low energy x-ray irradiation (circles), under 6 MeV beam irradiation (triangles) are reported, showing a high electrical resistivity (>10^{12} Ωcm) and good photoresponse to x-rays, with a sensitivity/mass ratio which is 20 times higher for diamond tips than for a standard ionisation chamber[3].

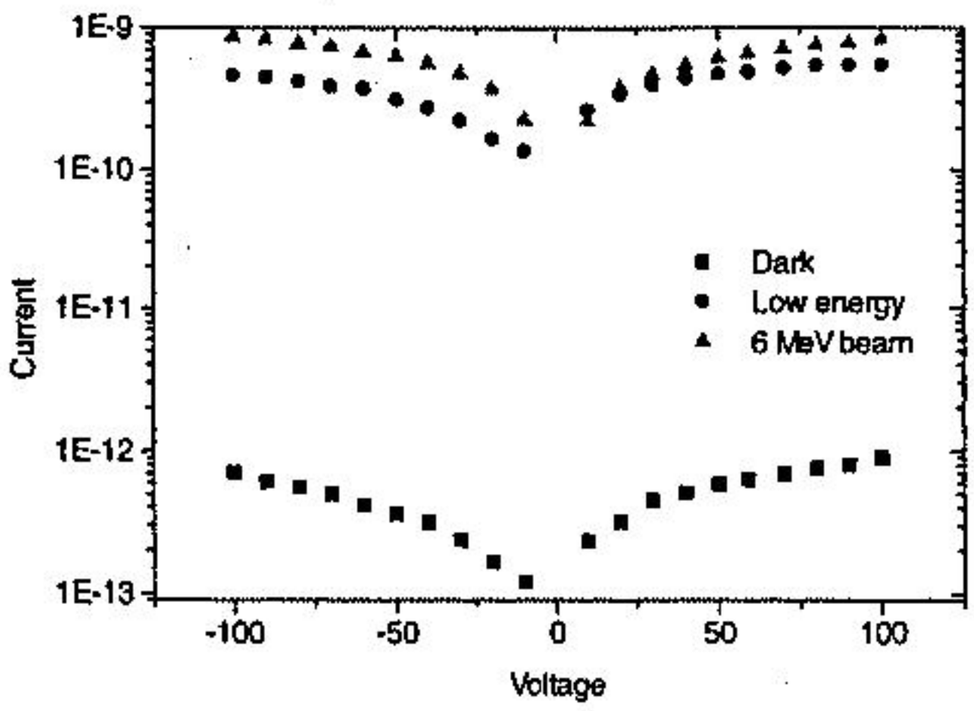


Fig. 6 Current-voltage characteristics of a diamond tip in dark (squares), under low energy x-ray irradiation (circle), under 6 MeV irradiation (triangles)

4. CONCLUSIONS

CVD diamond films have been successfully grown on tungsten wires and tips in a HFCVD apparatus. From SEM analysis, which has already been reported in Ref. 10, we see that the covering is uniform just after 6 hours deposition. SEM studies pointed out the relationship between growth rate and grain size and morphology and growth parameters. Actually, growth rate and size showed to be a decreasing function of wire diameter, whereas growth rate showed to be an increasing function of methane concentration. Increasing methane concentration however led to a worse quality of the film, as shown by morphology[9]. Micro-Raman spectra partly confirmed SEM observations: if the ratio of the area under the diamond peak against the sums of the areas of the diamond and of the non-diamond features may be considered a good index of the diamond quality, it looks as if best films can be made starting from low pressure (15 mbar), low methane content (≤ 0.25%), and small wire diameter (≤ 50 μm); however, a comparison with growth rates leads us to think that best diamond to non-diamond ratio can be found in thicker films, which is a reasonable guess. Nevertheless, comparisons with growth rate as a function of methane content shows an opposite trend, thus confirming the conclusion about the film quality getting worse with increasing methane content. Unfortunately, not so many conclusions may be drawn from the study of the diamond peak FWHM: we can say from the values that they are comparable to other CVD films, but it is actually difficult to find correlations with crystal domain and grain size as estimated by SEM and electrical measurements[10]. Generally speaking, the "diamond quality" of the films, as inferred from micro-Raman spectra, is good.

Characterisations of deposition have been shown useful for the evaluation of the suitable parameters for the growth of high resistivity films on wires and tips for detection purposes. Although we had to have a compromise between film quality as pointed out by SEM and micro-Raman measurements, manageabilty and high volume resistance as required by detectors applications, measurements under x-ray irradiation gave results comparable to standard ionisation chambers of a much larger volume. That makes CVD diamond films grown on wires and tips promising for future dosimetry applications.

5. REFERENCES

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