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Radiation damage to amorphous carbon thin films irradiated by multiple 46.9-nm laser shots below the single-shot damage threshold

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High-surface-quality amorphous carbon (a-C) optical coatings with a thickness of 45 nm, deposited by magnetron sputtering on a silicon substrate, were irradiated by the focused beam of capillary-discharge Ne-like Ar XUV laser (CDL = capillary-discharge laser; XUV = extreme ultraviolet, i.e., wavelengths below 100 nm). The laser wavelength and pulse duration were 46.9 nm and 1.7 ns, respectively. The laser beam was focused onto the sample surface by a spherical Sc/Si multilayer mirror with a total reflectivity of about 30%. The laser pulse energy was varied from 0.4 μJ to 40 μJ on the sample surface. The irradiation was carried out at five fluence levels between 0.1 J/cm^2 and 10 J/cm^2, accumulating five different series of shots, i.e., 1, 5, 10, 20 and 40. The damage to the a-C thin layer was investigated by atomic force microscopy (AFM) and Nomarski differential interference contrast (DIC) optical microscopy. The dependence of the single-shot-damaged area on pulse energy makes it possible to determine a beam spot diameter in the focus. Its value was found to be equal to (23.3±3.0) μm using AFM data, assuming the beam to have a Gaussian profile. Such a plot can also be used for a determination of single-shot damage threshold in a-C. A single-shot threshold value of 1.1 J/cm^2 was found. Investigating the consequences of the multiple-shot exposure, it has been found that an accumulation of 10, 20 and 40 shots at a fluence of 0.5 J/cm^2, i.e., below the single-shot damage threshold, causes irreversible changes of thin a-C layers which can be registered by both the AFM and the DIC microscopy. In the center of the damaged area, AFM shows a-C removal to a maximum depth of 0.3, 1.2 and 1.5 nm for 10-, 20- and 40-shot exposure, respectively. A Raman micro-probe does not indicate any change in the structure of the remaining a-C material. The erosive behavior reported here contrasts with the material expansion observed earlier [L. Juha et al., Proc. SPIE **5917**, 91 (2005)] on an a-C sample irradiated by a large number of femtosecond pulses of XUV high-order harmonics (HHs).

I. INTRODUCTION

Next generation short-wavelength free-electron lasers (FEL) are either already working in user mode (Free-electron LASer in Hamburg - FLASH, earlier known as VUV FEL and TTF1 FEL) or are under construction (LCLS in Stanford, XFEL in Hamburg). Operation of these facilities could be seriously limited by radiation-induced damage to mirrors manipulating the output beam. Grazing-incidence mirrors coated with amorphous-carbon films[1-4] seem to be suitable not only for the operating conditions of the FLASH facility (6 nm < λ < 60 nm, $\tau \sim 10$ fs, $E_{pulse} \sim 50$ μJ) but also for future facilities (e.g., LCLS and XFEL) working at even shorter wavelengths ($E_{phot} \sim$ 1-10 keV).

The XUV/X-ray radiation stability of a-C coatings was first investigated with a soft X-ray laser (sub-100-ps pulses of 21.2-nm radiation) at a relatively high fluence, i.e., ~ 1 J/cm^2. [5] However, the FLASH grazing incidence optics will be exposed to the short-wavelength radiation at a much lower fluence (~ 10 μJ/cm^2) but for longer periods. It is thus necessary to carry out experiments to investigate the consequences of prolonged irradiation at relatively low fluence. An XUV high-order harmonic (HH) beam was used as a source of short-wavelength radiation delivering high-energy photons to surfaces at a low single-shot fluence (well below the expected single-shot damage threshold), but with a high-average power due to the high repetition rate of the Ti:Sapphire laser.[6] In this contribution we are investigating the damage to the a-C optical coating when the XUV laser fluence is set to half the single-shot damage threshold and several tens of shots are accumulated. The capillary discharge Ne-like Ar laser at 46.9 nm [7,8] was chosen for this experiment because of its high pulse energy, allowing us to easily achieve fluences in the vicinity of the single shot damage threshold, and an excellent shot-to-shot stability of the output power [9], ensuring that no shot in the irradiation series would overcome the single-shot damage threshold due to the shot-to-shot fluctuations of pulse energy.

The material damage induced by a single shot of such a laser has already been studied in metallic alloys [10], Sc/Si multilayers [11], organic polymers [12] and ionic crystals [13]. Observation and investigation of the damage induced by multiple shots of the XUV laser below the single-shot damage threshold are, according to our best knowledge, reported for the first time in this contribution.

II. EXPERIMENTAL

The samples used for testing the radiation stability of amorphous carbon optical coatings were (40-45)-nm thin a-C layers deposited on silicon substrates by GKSS (Geesthacht, Germany). The standard thickness of the coating has been kept constant since the initial experiments focused on the short-wavelength laser-induced damage [2] because of an influence of the substrate on the substantial damage of the thin layer. The amorphous carbon films were produced on planar, well-polished silicon substrates in an ultrahigh-vacuum chamber by DC magnetron sputtering. The deposition equipment comprised two magnetron sources with diameters of 3 inches. The water-cooled substrate holder was rotated in order to achieve uniform film thickness. A computer-driven shutter between the target and substrate controlled the deposition time. The deposition rates were varied between 0.02 and 0.2 nm/s. The sputtering gas was high purity argon (99.99999 %; Argon 7.0 purchased from Messer, Germany) with a typical pressure between 0.1 and 0.3 Pa. The background pressure in the deposition chamber was less than 10^{-5} Pa. The films were routinely characterized in the lab with unpolarized Cu-Kα radiation using an X-ray reflectometer (Bruker AXS D8) equipped with a reflectometry stage and a primary Göbel mirror. The reflectometry curves were fitted using the Bruker AXS simulation software. Both film thickness and density were determined. Furthermore, the film properties were measured at relevant wavelengths in the XUV and soft X-ray range at the soft X-ray reflectometry beamline

G1 at HASYLAB/DESY. This reflectometer covers an energy range between 40 and 1200 eV. The beam size at the sample surface is 0.85 mm x 2.2 mm. The energy resolution is 1/140 - 1/200. The radiation at G1 is s-polarized and the measured signals are normalized to the incoming flux. The flux on the sample surface is between 2×10^9 and 2×10^{11} photons/(100 mA ΔE s). The reflectometry curves were simulated using D. L. Windt's IMD (Version 4.1.1) software, which ran on the IDL (Version 5.2) platform. The simulations were used to determine key a-C film properties such as thickness and roughness. Raman spectroscopy provided an estimate of the fraction of sp^3 carbon atoms in the a-C coating, i.e., $[sp^3]/([sp^2]+[sp^3])=0.17$. For more details on production and characterization of the samples see [1-3,14].

The amorphous carbon (a-C) sample was placed in the vacuum interaction chamber and irradiated by the focused beam of a capillary-discharge Ne-like Ar XUV laser at the University of L'Aquila [8,9,13], see Fig. 1. The laser wavelength and pulse duration were of 46.9 nm and 1.7 ns, respectively. The repetition rate of the CDL device was 0.2 Hz. Since energy content of each pulse should be recorded in our experiments, a well-defined part of the beam is reflected towards the vacuum photodiode by a Lloyd's mirror located 90 cm from CDL output. The rest of the laser beam was then focused onto the sample surface by a spherical Sc/Si multilayer mirror placed at a distance of 130 cm from the source. The total reflectivity of the focusing mirror was about 30% at the laser wavelength. The broad-band incoherent UV-Vis radiation emitted from the plasma column of the capillary discharge may be reflected by such a mirror with a comparable efficiency, i.e., 30-40 %. [15] The axis of the spherical Sc/Si multilayer mirror (focal length = 8 cm, diameter = 1.6 cm) was turned about 5° with respect to the axis of the incoming beam in the horizontal plane of the experiment. Taking into account the mirror reflectivity and other losses during the beam characterization and manipulation, the laser pulse energy on the sample surface was about 20% of the laser output. Five fluence levels were adjusted by changing the pulse energy to 0.4 μJ, 2.0 μJ, 8 μJ, 20 μJ, and 40 μJ while other irradiation parameters remained unchanged. The irradiation was carried out under normal incidence conditions at the five fluence levels accumulating five different numbers of shots, i.e., 1, 5, 10, 20, and 40, at each fluence. A control of the shot-to-shot fluctuation of pulse energy was conducted with the vacuum photodiode recording a portion of total beam energy reflected by the Lloyd's mirror. Fluctuations did not exceed 20% at any fluence level.

Irradiated surfaces were investigated using a Nomarski optical microscope (BX51M DIC microscope, Olympus; Japan) and by an AFM microscope working in tapping mode (D3100 NanoScope Dimension controlled by NanoScope IV Control Station, Veeco; USA). To study structural changes possibly induced in the a-C layer by XUV-laser radiation Raman measurements were performed, in the usual back scattering geometry, with a Raman spectometer (Renishaw Ramascope; UK) equipped with a CCD camera and a Leica microscope DMLP. Typically, Ar^+ laser (514.5 nm) spots with diameter of 4 μm were used. This tool enabled us to probe selected locations on the sample surface.

III. RESULTS AND DISCUSSION

DIC micrographs of the damage patterns induced by a single laser shot at increasing pulse energies can be seen in Fig. 2. In Figs 2a,b, a-C layer expansion and removal create the damage pattern; damage to the silicon substrate can be indicated at the highest fluence, i.e., in Fig. 2c. The dependence of damaged surface area on laser pulse energy is displayed in Fig. 3. Liu's technique [16,17] was used for the analysis. Applying this technique, a single-shot damage threshold and focal spot radius were determined. The slope of the fitting line represents the focal spot area. The cross-section of the fitting line with x-axis gives the threshold energy, i.e., an energy at which the damaged area is equal to zero. Dividing the threshold energy by the focal spot area provides the threshold fluence. The focal spot diameter was found to be equal to (23.3±3.0) μm. A threshold fluence of 1.1 J/cm^2 was then determined for the single-shot exposure. In this spectral region, the single-shot damage threshold of a-C thin layer was determined only for femtosecond pulses of 32.5-nm free-electron laser radiation. [18] A threshold of 0.06 J/cm^2 was found [18], using a very similar experimental procedure as described above. Since the single-shot threshold is generally controlled by a rate of deposited energy density, the difference between 1.1 J/cm^2 and 0.06 J/cm^2 might be explained by different pulse durations, i.e., one nanosecond and twenty five femtoseconds, respectively. Morphological changes connected with the damage were in both cases represented by extrusions of graphitized carbon.

Since Liu's technique assumes a Gaussian beam profile, the values related to the focal spot may not be accurate if the radiation intensity distribution in the CDL beam is different. Although the focal spot area is used to calculate all fluences, for the present experiment it is important just to indicate a fluence well below the single-shot damage threshold. The ratio of the threshold and sub-threshold values will not be affected by any prospective correction made to the focal spot area.

The AFM image (Fig.4a) shows material extrusion and almost complete removal of the carbonaceous coating from silicon substrate when the sample was irradiated above the single-shot damage threshold. Raman spectra of such a sample are shown in Fig. 4b. Typical Raman spectra of a-C have, at 1530 cm^{-1}, a shape with two overlapping bands – a high-frequency G-band and low-frequency D-band. An increase in the D-band is indicative of the increasing amount of sp^2 bonds in the material. [19] In Fig. 4b (blue line), a remarkable increase of D-band can be seen in the expanded material remaining in the damaged area. It indicates a high degree of graphitization in the a-C layer damaged by a single shot of XUV-laser radiation. Even at the boundary of the damaged area (Fig. 4b - black line), where it is hard to see any surface change by microscopy, the band peaking at 1530 cm^{-1} broadens in comparison with the spectrum of pristine material (Fig. 4b - red line) due to the beginning of graphitization.

At the fluence under 1.1 J/cm^2 we do not see any damage to the surface irradiated by a single shot. However, damage appears when the sample was irradiated by ten and more shots at a fluence of 0.5 J/cm^2. The nature of this damage can be recognized in Fig. 5. The irradiated region of amorphous carbon was eroded. A shallow but clearly developed crater was formed in the material. Its elongated shape is likely due to an astigmatism in the beam focusing. In the center of the damaged area, AFM shows a-C removal to a maximum depth of 0.3, 1.2 and 1.5 nm for 10-, 20- and 40-shot exposure, respectively. The DIC microscope did not show any damage to the surface irradiated by 5 shots at a fluence of 0.5 J/cm^2. At a fluence of 0.1 J/cm^2, an accumulation of 40 shots did not lead to any damage, although the total exposure is 4 J/cm^2. This is almost the same value as 5 J/cm^2, estimated for 10-shot exposure at a single-shot fluence of 0.5 J/cm^2, which results in the damage visualized by our microscopes (Fig. 5a). This implicates that the multiple-shot damage process could be dependent not only on the total dose of 26.4-eV photons but also on the single-shot laser fluence. Further experiments are in progress to prove the existence of such dependence.

At a certain fluence below the single-shot damage threshold, there is a minimum total exposure, i.e., dose delivered by the number of laser shots leading to the surface damage which can be registered by the chosen method of surface analysis. This multiple-shot damage threshold is strongly influenced by the sensitivity of the analytical technique used for the registration of mild irreversible changes on the surface. Contrary to this, the single-shot damage threshold is defined as a minimum single-shot fluence causing an observable irreversible change which is qualitatively similar to the damage observed at fluences well above the threshold. Usually, such a threshold is determined by an extrapolation as described above (see, please, Fig. 3). This is the reason, why the threshold does not depend much on the sensitivity of the method utilized for the surface analysis. Recently, we published a model connecting these damage modes to describe both the desorption and the ablation behavior of organic molecular solids irradiated by the soft x-ray radiation. [20] However, it is quite complicated to create such a model for the amorphous carbon because the low-fluence multiple-shot exposure leads to the material removal while the high-fluence single-shot irradiation results mostly in an expansion. The work on the complex model is in progress.

This erosive behavior reported here contrasts with the material expansion observed on the a-C sample irradiated by a large number of femtosecond pulses of XUV high-order harmonics. [6] The total exposure, i.e., 2.4-7.2 J/cm^2 and 5-19.2 J/cm^2 for HHs and CDL, respectively, is almost the same in both the cases. The difference can be found in the maximum intensity of XUV radiation, i.e., 5 GW/cm^2 and 0.3 GW/cm^2 for HHs and CDL, respectively. HH wavelengths are also a bit longer (53 nm, 62 nm, and 73 nm) than 46.9 nm of CDL. There are two possible explanations for the different behavior: (1) higher local dose rate achieved with the HH beam makes the material tend towards expansion, i.e., graphitization, and (2) a dual action of incoherent long-wavelength plasma radiation and coherent XUV radiation, both emitted by the capillary discharge, in the a-C layer. Short-wavelength radiation cuts the material into tiny pieces whilst long-wavelength radiation heats up the surface releasing volatile fragments into vacuum. Such an explanation was recently given [21] for the enhancement of PMMA erosion simultaneously induced by soft X-rays and long-wavelength UV-Vis radiation emitted from laser-produced plasma.

Raman spectra of the material remaining at the bottom of the crater (its image can be seen in Fig. 5c) are shown in Fig 6. The Raman composed band at 1530 cm^{-1}, whose shape provides information on the ratio of graphite - sp^2 and diamond - sp^3 bonds, did not show any change.

Another difference appears here compared to HH irradiation. There is no trace of the photoluminescence detected in the background of the Raman signal taken from a-C layers irradiated by high-order harmonics. [6] Such luminescence is characteristic of a-C layers with low micro-hardness, indicating a very early stage in the graphitization process. In conclusion, no modification of the a-C structure can be seen in the interior of the craters formed by multiple-shot exposure with the XUV laser.

The damage observed on the surfaces irradiated by many accumulated shots below the single-shot damage threshold is likely due to a radiolytic cleavage of C-C bonds induced by individual 26.4-eV photons. CDL radiation is under the given irradiation conditions able to decompose the carbonaceous material into tiny pieces that are able to leave the irradiated surface into vacuum. The radiation-initiated (i.e., radiolytic) damage to the material structure, as originally suggested by Deacon [22], has been demonstrated with synchrotron radiation as direct photo-etching [23,24] as well as material expansion. [24]

The observed erosion of a-C material, which is not accompanied by any structural change in the near-surface region of the irradiated material, could be used for direct nano-structuring of surfaces. Surface irradiation by multiple shots slightly below the single-shot damage threshold ensures the absence of any undesirable structural change in and below the structure created at relatively high etch rate. This combination is hard to achieve with synchrotron radiation sources and single-shot XUV-laser ablation would alter surrounding material, especially for radiation resistant materials.

The lack of an observed change in the sp^3/sp^2 ratio is in contrast with the results of irradiating such materials with certain X-rays. [25,26] Irradiation of hydrogenated a-C by ~10 keV synchrotron radiation [25] results in an increase in the sp^3 fraction. Contrary to that, sp^3-to-sp^2 conversion occurs in tetrahedral a-C (ta-C) irradiated at the carbon K-edge (the 1s threshold at 280-300 eV).

[26] However, irradiation by 250 eV photons, i.e., well below the K-edge, does not initiate any change in ta-C structure. [26] This is in a good agreement with our finding from the experiment conducted with 26.4-eV photons.

IV. CONCLUSIONS

It has been clearly demonstrated that XUV-laser radiation can damage a-C layers exposed to tens of shots at a fluence of about half the single-shot damage threshold. This damage likely occurs by photo-induced erosion of irradiated material. Each photon of the radiation emitted by the laser used in the present study carries enough energy to break any C-C bond. Multiple energetic photons cause a decomposition of carbonaceous matter leading to the formation of small fragments desorbed from irradiated surface into the vacuum. No structural change of a-C was found by the Raman microprobe in the damaged area. It supports the key role of non-thermal processes in damaging a-C optical coatings irradiated by many XUV-laser shots below the single-shot damage threshold. These results seem to be important for estimating mechanisms of the damage to surfaces of highly irradiated optical elements developed for manipulating ultra-intense XUV/X-ray beams provided by next generation sources (FLASH and XFEL in Hamburg; LCLS in Stanford), because most of the damage investigations were so far carried out in the single-shot mode. In addition to the optics issue, the observed phenomenon could be used for direct, single-step nano-patterning of technically important materials. A processing technique based on this phenomenon could be soft (i.e., not altering the material of the resulting micro-structure) yet efficient.

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Figure captions

FIG. 1. Experimental layout for a-C irradiation by a focused beam from a capillary-discharge Ne-like Ar laser (not to scale).

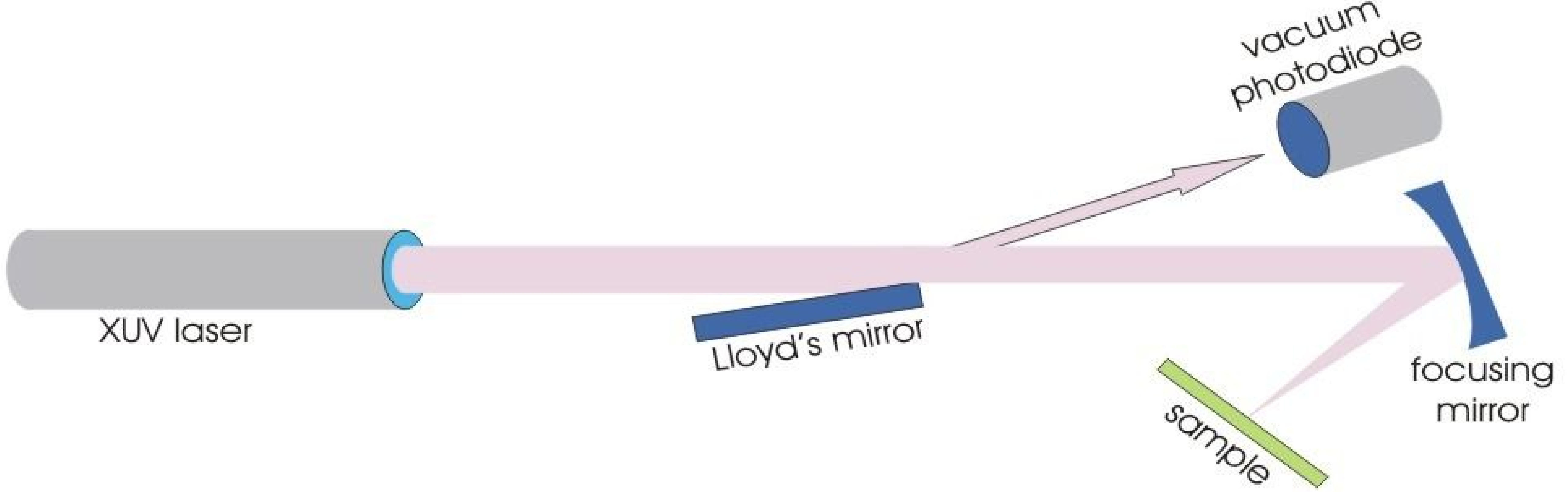
FIG. 2. DIC micrographs of a-C coating irradiated by a single shot provided by the XUV laser. The laser fluence increases from the left to the right – 1.9 J/cm^2, 4.7 J/cm^2, and 9.4 J/cm^2. Whole scale-bar represents 20 μm.

FIG. 3. Dependence of the damaged surface area on laser pulse energy.

FIG. 4. (a) AFM image and (b) Raman spectra of the a-C sample irradiated by the focused XUV-laser beam (single-shot exposure) at a fluence of 1.9 J/cm^2 , i.e., above the single-shot damage threshold. Red line: spectrum of pristine, unirradiated material; black line: spectrum taken in the close vicinity to the damaged area; blue line: spectrum of expanded, severe damaged a-C layer. The spectra were normalized and then moved to avoid their overlap.

FIG. 5. Topographic AFM images of the a-C surface exposed at a fluence of 0.5 J/cm^2 to (a) 10, (b) 20, and (c) 40 laser shots; (d) profiles measured in the maximum depth of the craters. Each AFM image is of 30 μm x 30 μm; the lateral resolution is of (a),(c) 85 scans / 10 μm and (b) 64 scans / 10 μm.

FIG. 6. Raman spectra taken in and out of the crater formed in a-C exposed to 40 XUV-laser shots at a fluence of 0.5 J/cm^2, i.e., below the single-shot damage threshold. The spectra were normalized and then moved to avoid their overlap.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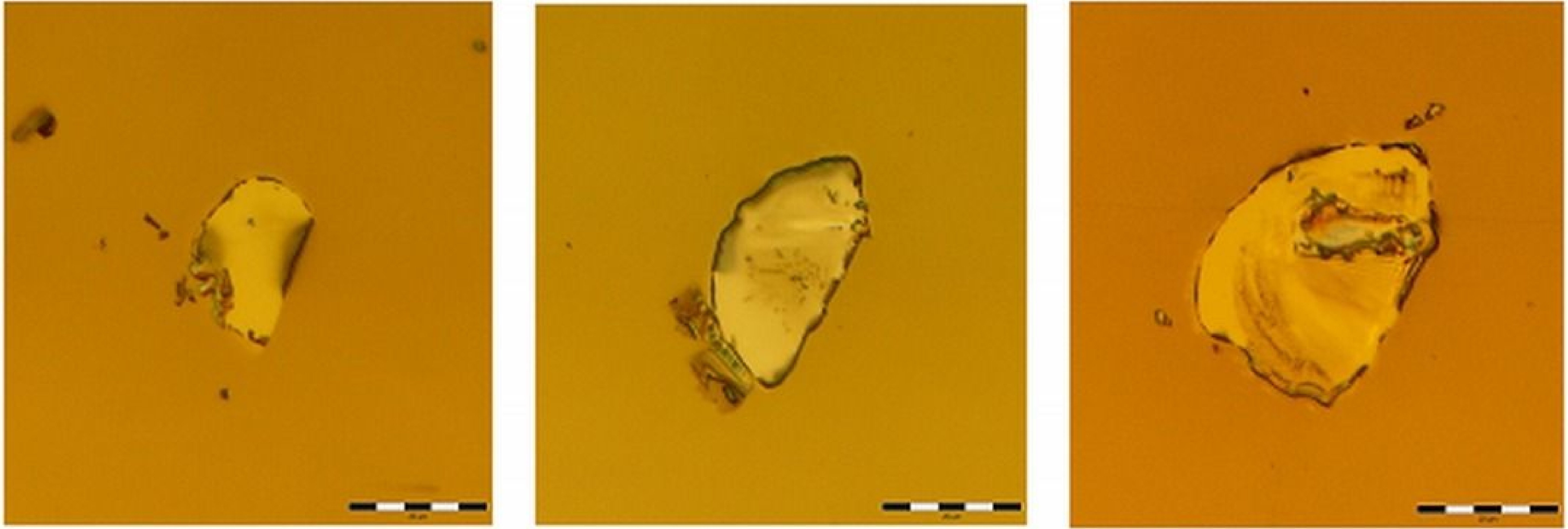
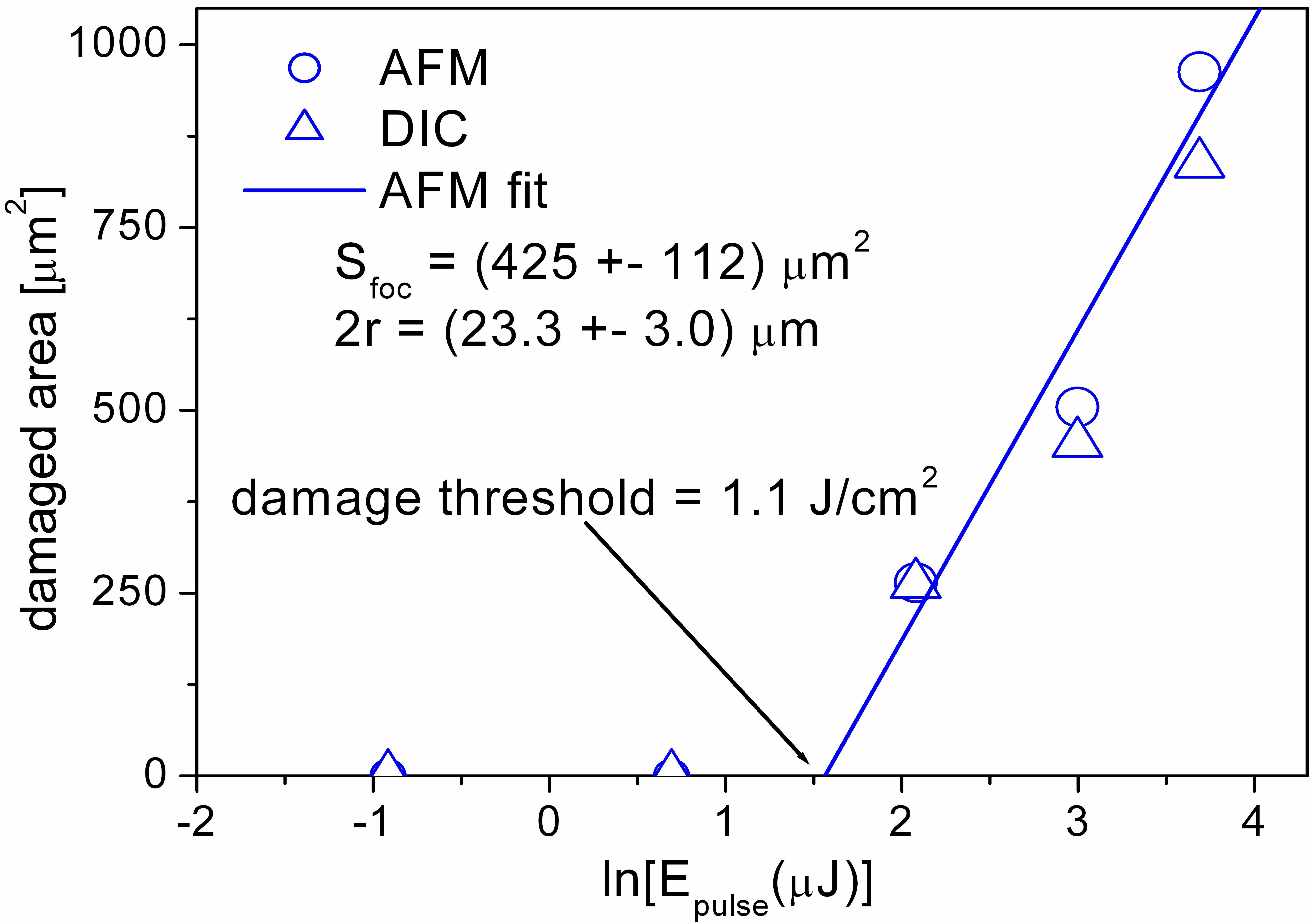
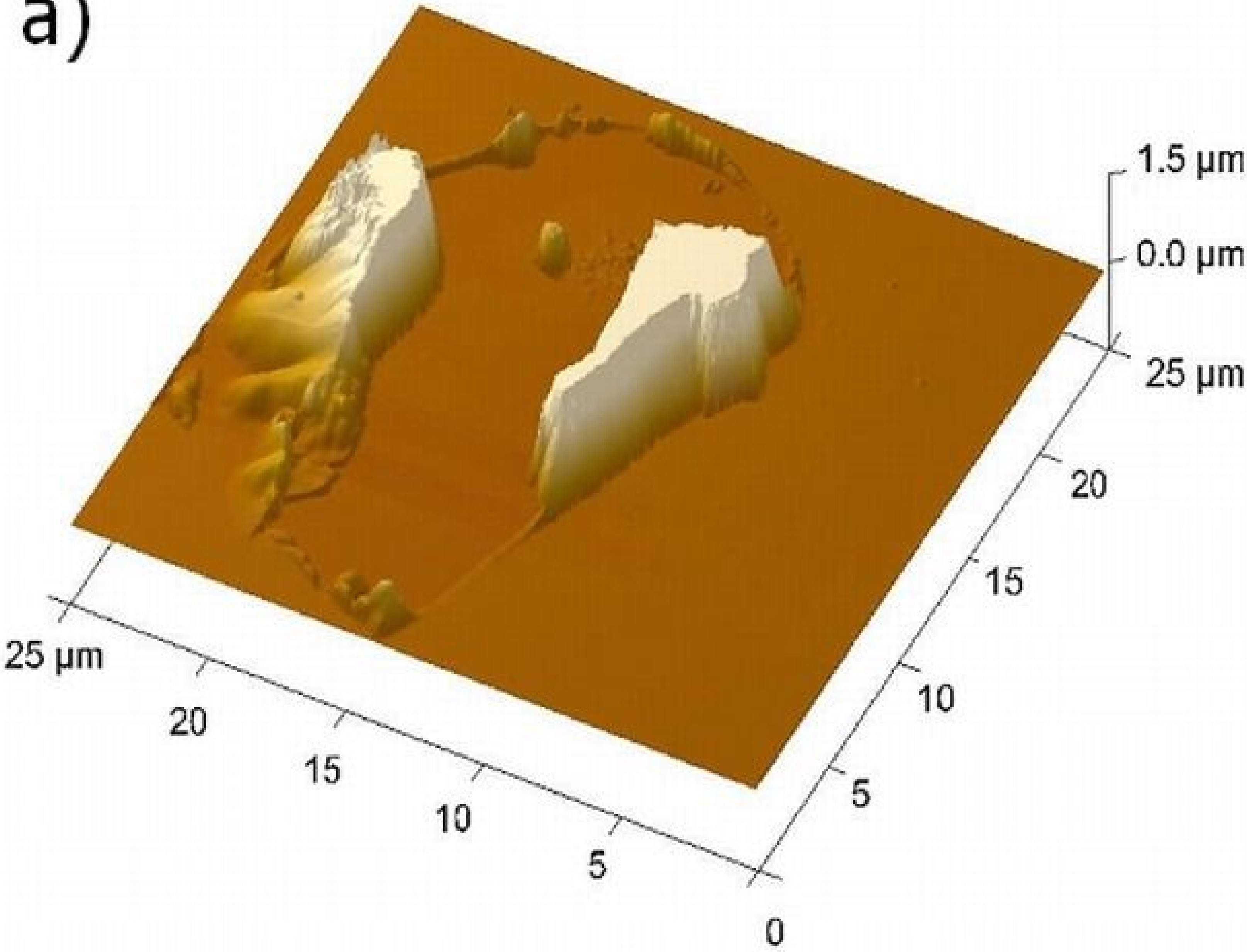


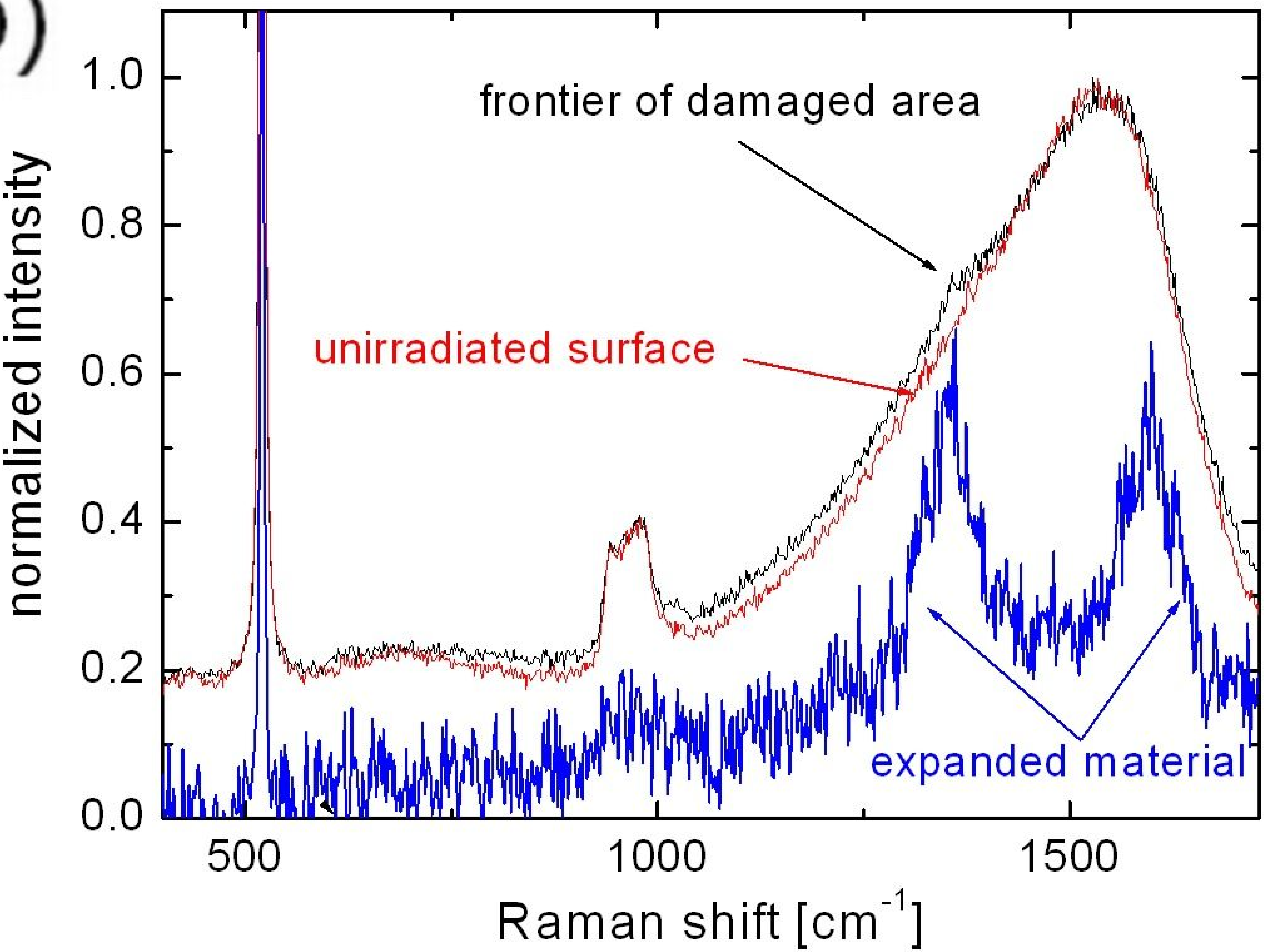


AFM
DIC
AFM fit
S_foc = (425 +- 112) μm²
2r = (23.3 +- 3.0) μm
damage threshold = 1.1 J/cm²
damaged area [μm²]
ln[E_pulse(μJ)]
1000
750
500
250
0
-2
-1
0
1
2
3
4

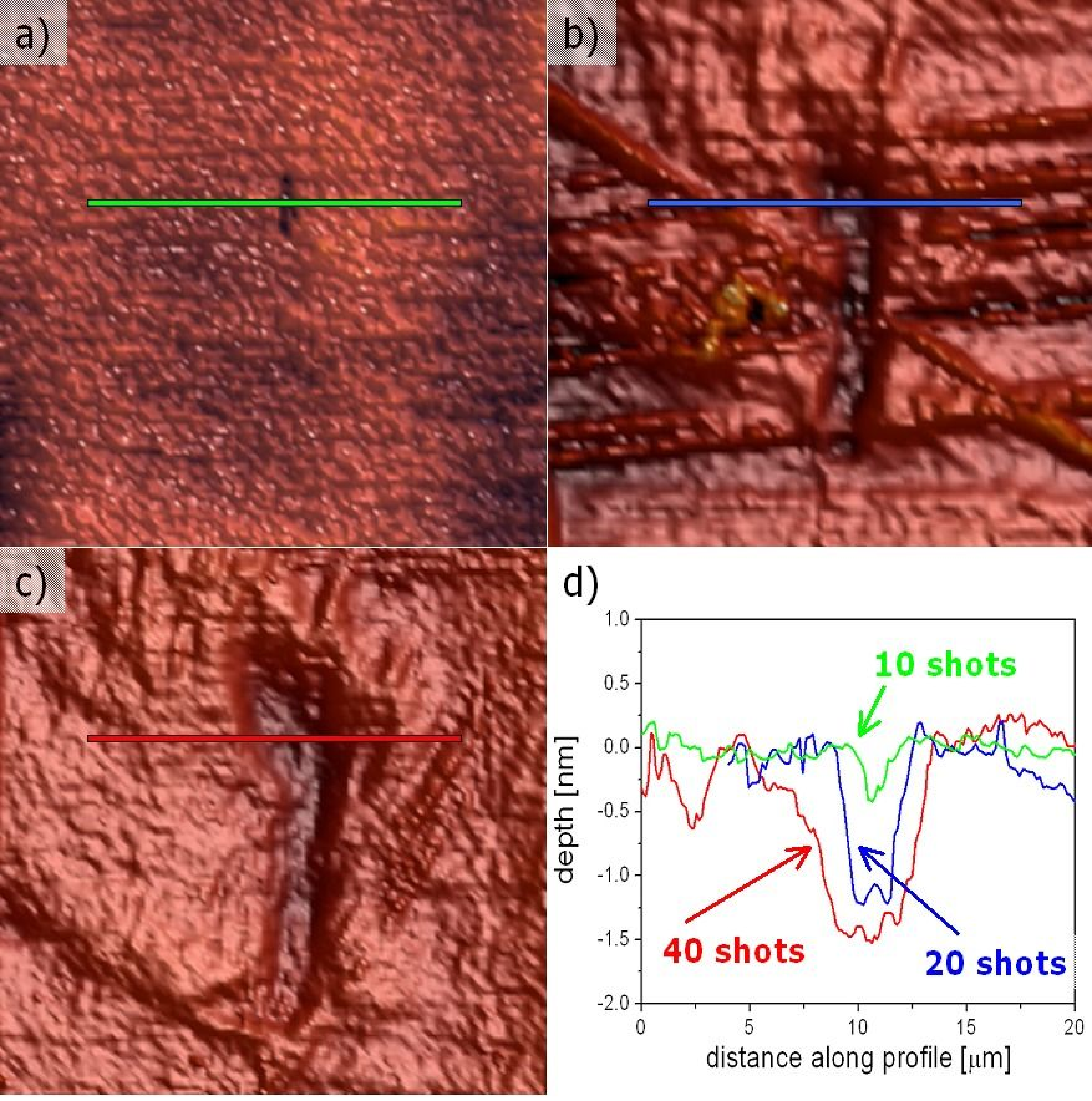
a)

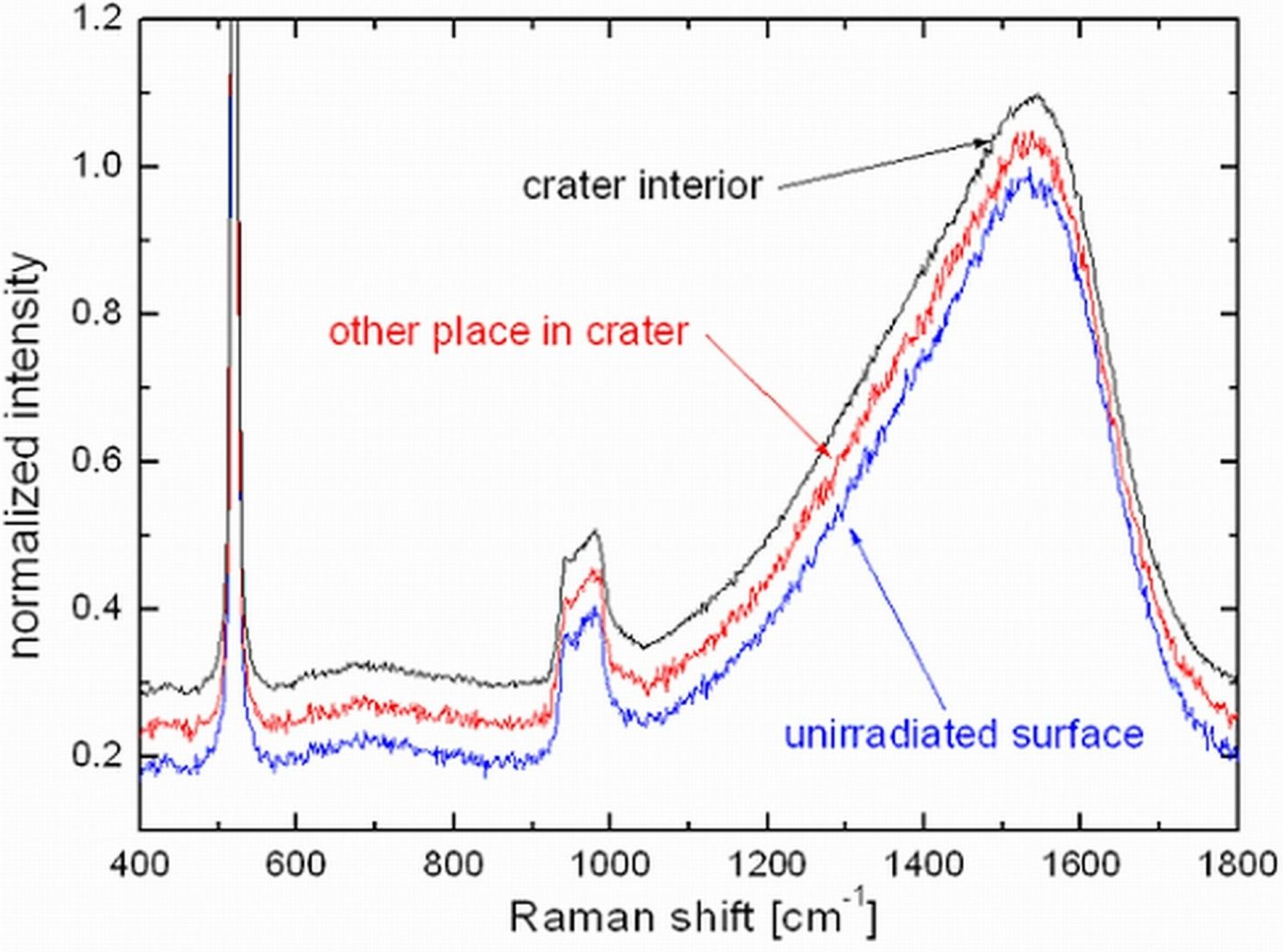


b)



1.0
0.8
0.6
0.4
0.2
0.0
normalized intensity
500
1000
1500
Raman shift [cm-1]
frontier of damaged area
unirradiated surface
expanded material


a)
b)
c)
d)
10 shots
20 shots
40 shots
depth [nm]
distance along profile [μm]
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0
5
10
15
20



1.2
1.0
0.8
0.6
0.4
0.2
normalized intensity
crater interior
other place in crater
unirradiated surface
400
600
800
1000
1200
1400
1600
1800
Raman shift [cm^{-1}]