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S. Lazare, F.Weisbuch, V. Tokarev, D.Débarre Presented at the Fifth International Symposium on Laser Precision Microfabrication, edited by Isamu Miyamoto, Henry Helvajian, Kazuyoshi Itoh, Kojiro F. Kobayashi, Andreas Ostendorf, Koji Sugioka, Proceedings of SPIE Vol. 5662 (SPIE, Bellingham, WA, 2004) 249-254.

Improved resolution of submicron KrF laser ablation of polymers by a new filtered imaging irradiation

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ABSTRACT

Surface grating-like ablation with microscopic period (Λ~1-5 µm) is achieved at the surface of polymers with the aid of the KrF laser patterned with a mask projection technique using a precision imaging lens. The ablated patterns can be controlled with a submicron accuracy in most cases on smooth polymer surfaces. Prediction of these patterns can furthermore be made with the aid of theoretical models combining ablation curves, intensity profiles and hydrodynamic flow. We further demonstrate that by using harmonic filtering the grating period can be divided by a factor 2 thus leading to a convenient resolution enhancement. This improvement can be achieved by two experimental approaches. One is by changing the defocus and the other is the removal of low level orders (0 and ± 1) of the Fourier components of the image beams. Resulting grating patterns with doubled spatial frequency will be presented for a number of polymeric materials (AFM, SEM). It reveals to be a good method to overcome the theoretical limitations due to numerical aperture of the precision lens which prevent the transfer of details in the image by erasing the high spatial frequencies. This interesting optical set up and method offer also the advantage of a large working distance above the sample surface which is compatible with irradiations in vacuum and liquid phase.

Keywords: Materials, laser, precision projection lens, filtering, grating, resolution, mechanisms, microscopy, polymer

1. INTRODUCTION

Exploring the potentially high spatial resolution of laser ablation is a challenging scientific goal and is of great technological interest. In a recent paper [1] we have shown that KrF laser ablation on the surface of various polymers is a process of submicron resolution if a precision lens system is used to project the image of a mask on the surface of the treated material. However the complex mechanisms of the material removal is not fully understood despite the large body of theoretical and experimental work achieved since the development of the laser ablation concept more than 20 years ago [2,3]. Therefore experiencing with microbeams is an interesting way to try gaining some more detailed knowledge about the material removal by looking at ablation profile, nanoparticles, liquid formation, etc.. . With the submicron ablation set-up, we have evidenced and modelled new features of the ablation mechanisms, like transient liquid flow on the surface of PET (Mylar) during a single pulse KrF laser ablation [4,5]. In the present paper we report two new experiments using the precision lens laser ablation system that are aimed at doubling and quadrupling the resolution of the ablation patterns (essentially gratings). In the previous experiments of reference [1] we used chrome-on-quartz grating masks which projected an image grating of period 3.7 µm and 2.1 µm. In these new experiments we use the same masks but use two different experimental procedures : 1) the first one uses "defocus adjustment" in which the defocus is purposely varied in order to look for the appropriate and distorted image intensity profile and 2) the second one uses "diffraction order filtering" in order to select two conjugated orders (±n) and let them interfere at the image level to get a sine type intensity modulation with increased spatial frequency. We show that for a number of usual polymers (PC, PET, PEN, PI-Upilex), chosen for their original surface quality, gratings with submicron period are successfully obtained by ablation with a single pulse of the KrF laser. The perspectives opened by such results are discussed.

2. PRECISION LENS EXPERIMENTS FOR IMPROVED RESOLUTION

The selected polymer samples were chosen because of their good optical and surface qualities allowing an easy atomic force microscope measurement and optical microscope observation of the printed gratings. The polymers studied are polyimide (PI), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN) and bisphenol A polycarbonate (PC). Commercial names are Upilex for PI (Ube), Mylar D for PET, Teonex from Dupont-Teijin for PEN and PC samples from polycarbonate panels Axxis (DSM Engineering Products). The precision lens KrF laser ablation set-up was described in details in previous publications [1,6] and the basic procedure of Fourier imaging is not repeated here. Only the specific features of these following experiments are explained below. The ablated patterned were obtained for a single pulse in all experiments. The two experiments are possible only when the image position (defocus equals 0) has been carefully determined. SEM electronic microscopy and AFM near field scanning microscopy were used for surface analysis after ablation. Atomic force microscope (AFM) was either a Park Scientific Instr. (at IEF) or a Thermomicroscope CP Research (at LPCM). The analysis were done by using the contact mode with silicon Ultralever tips adjusted at the minimum the setpoint.

2.1 Two beams imaging experiments by filtering

The incident laser light is diffracted by grating mask into many beams identified by their diffraction order $\pm n$. The larger value of n correspond to beams of larger inclination with respect to the optical axis. Due to increasing inclination with n, only a limited number of beams (1-3 in our case) are entering the imaging lens and as a consequence after transmission reconstitute the projected image with loss of some details. In theory all diffracted beams are necessary to reconstitute a good image, but in reality the lens acts as a filter which transmits only low inclination beams, but looses high inclination beams responsible for the information on small details of the mask. By analogous filtering in the following experiment the idea is to allow the transmission by the imaging lens of only two beams of conjugated diffraction orders $\pm n$ by placing blocking paper masks directly on the lens. The image in this case is simply due the interference of these two beams and the period of the interference modulation depends only on $\pm n$ and the grating mask parameters. The fluence at the ablated sample surface [6] is given by:

$$F(x) = F_0 \frac{2\alpha_n^2}{\alpha_0^2 + \sum_{i=1}^{\infty} 2\alpha_i^2} (1 + \cos(2\pi \frac{2n}{p} x)) \qquad (1)$$

where F_0 is the fluence without mask, x is the position coordinate in the image plane, p is the period of the non filtered image of the mask and α_n^2 are the intensities of the diffraction orders, defined as :

$$\alpha_n^2 = (\sin(\pi \frac{p-a}{p} n) \Big/ \pi \frac{p-a}{p} n)^2 \qquad (2)$$

in which the mask parameter a is the spacing between black stripes, for instance: 1.4 µm for p=3.7 µm and 0.7 µm for p=2.1 µm. The equation (1) tells us that the spatial frequency of the interference modulation in the filtered image is now $2n/p$ or equivalently the new period is $p/2n$. By these experiments the resolution can be improved by a factor equal to $2n$.

2.2 Defocus adjustment experiments (3 beams)

In this experiment the n=0,±1 orders are selected by filtering similarly to the previous case and now the idea is to explore the intensity profile around the good image position (defocus z=0) by varying the defocus or the axial coordinate z . z is positive when the lens to sample distance is increased by definition. In practice the z variation is in the range of ~0-100 µm. It is shown by a Fourier optics calculation [6] that the intensity profile at the sample surface can be expressed by:

$$I(n,x,z) = 2\alpha_n^2 \cos(2\pi \frac{2n}{p} x) + 4\alpha_n \alpha_0 \cos(2\pi \frac{n}{p} x) \cos(\pi \frac{n^2 z \lambda}{p^2}) + \alpha_0^2 + 2\alpha_n^2 \qquad (3)$$

where λ is the laser wavelength (248 nm), n is equal to 1 (not ±1) and which holds true for small values of z ($|z|<100\mu m$). Equation (3) is of the form $I_1(x)+I_2(x,z)$+Const. where the two first terms are periodic functions of spatial coordinates x and the second also of z. The term of interest is the first one since its spatial frequency is $2n/p$ that is to say double of that of the mask image n/p which is represented by the second term. Due to the dependence on z the second term vanishes for a certain positions of defocus called $z_{1/2}$ and given by:

$$z_{1/2} = \frac{p^2}{2\lambda} \qquad (4)$$

which takes for instance for the mask period p=3.7 µm the value $z_{1/2}$= 27.6 µm. The two defocus positions $z = \pm z_{1/2}$ providing an intensity modulation in x with the doubled frequency were found experimentally. It is shown in 3.1 (Fig.1) that the ablated surfaces successfully reproduce these predictions.

3. RESULTS

3.1 Results of defocussing experiments

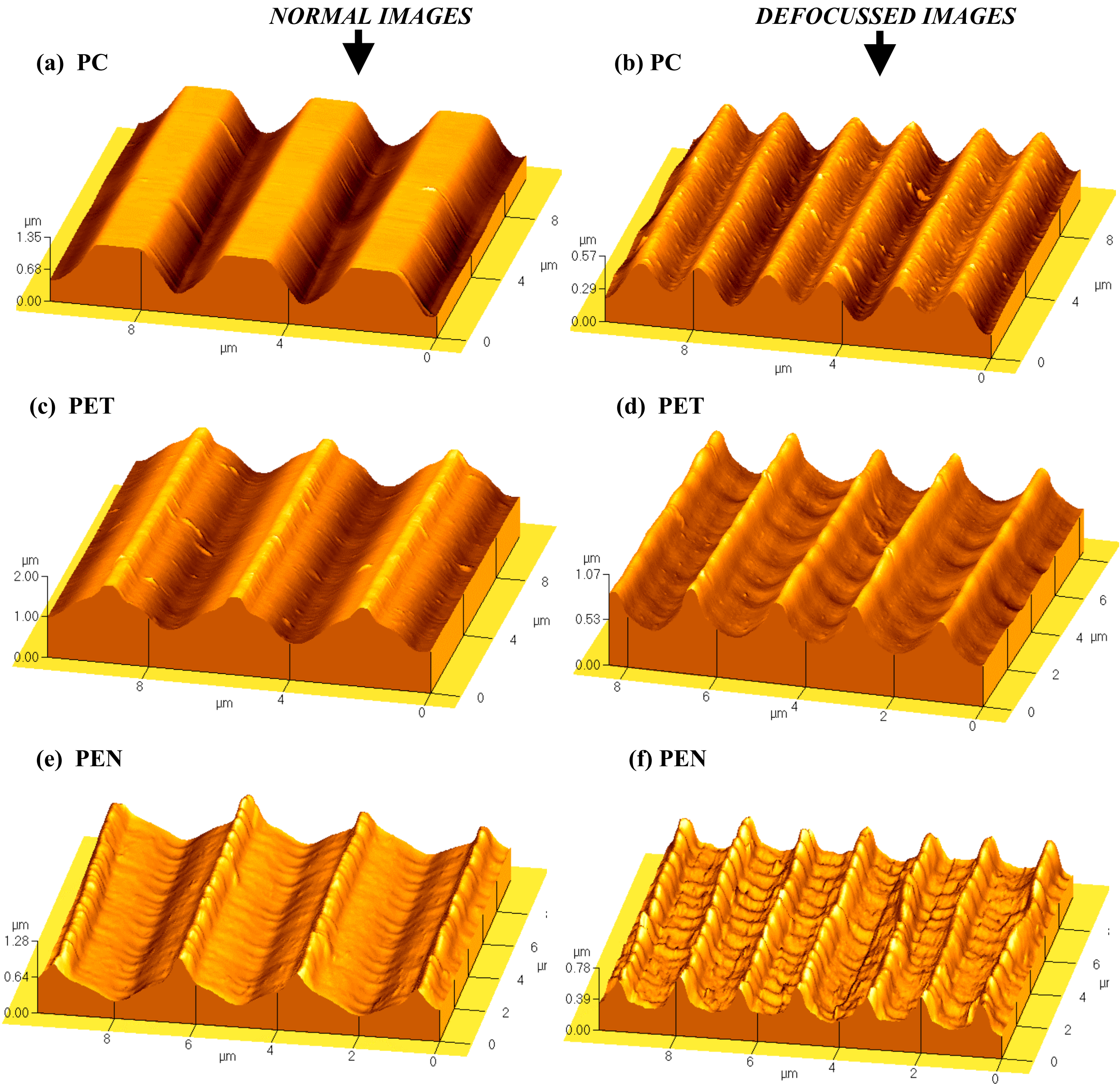

Fig.1 KrF laser ablated patterns by projection with a precision lens and measured by AFM. Defocussing experiments ($z_{1/2}$) images displaying a double spatial frequency for PC, PET and PEN (b,d,f) are displayed in the right-hand column. In the left-hand column (a,c,e) normal grating images for comparison. Normal periods are 3.7 µm for PC, PET and 3.0 µm for PEN. Irradiations were done with a single pulse of fluence F=1 J/cm² in air.

3.2 Results of 2 beams filtering experiments

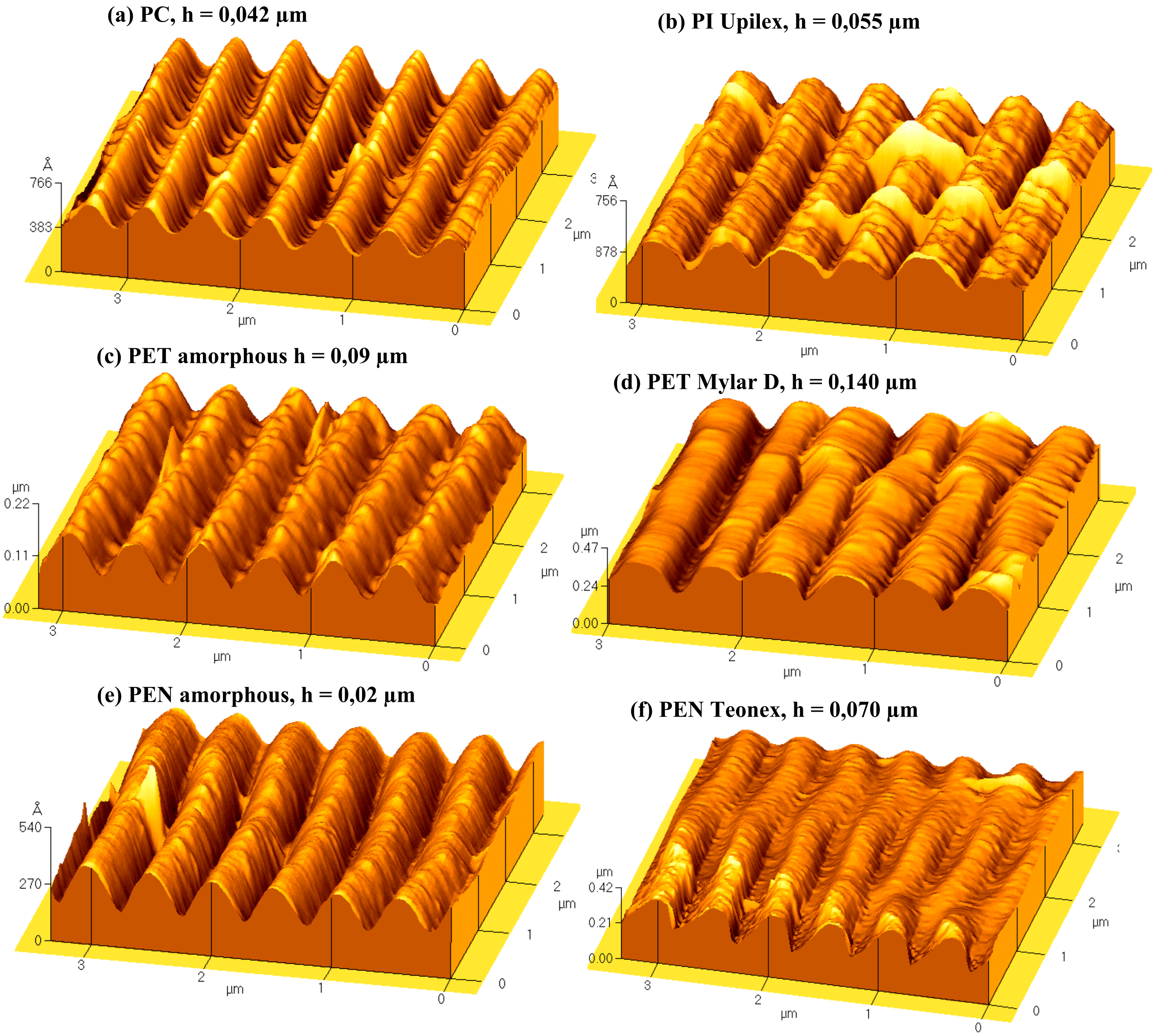

Fig.2 KrF laser ablation patterns obtained with the 2 beams filtering experiments described in 2.1, by using diffracted beams of orders ±2. The obtained period is 0.53 µm which corresponds to $p/4$ where p=2.1 µm is the period of the normal grating image (the spatial period is quadrupled).

Table 1 Ablation depths for the polymers irradiated with one pulse of fluence of 105 mJ/cm² used in these experiments.

	PEN	**$PEN_{amorph.}$**	**PET**	**$PET_{amorph.}$**	**PC**	**PI (Upilex)**
Theoretical depth (µm)	0,080	0,080	0,085	0,085	0,038	0,045
Experimental depth (µm)	0,07	0,02	0,14	0,09	0,042	0,055
Ablation threshold (mJ/cm²)	~25	~25	30	30	40	~50

The above AFM observations were confirmed with SEM images which are not presented here. They recorded images can be partially distorted by ablated redeposited products and particles. Some are strongly affected by the formation of a transient liquid film that can flow under the action of the ablation pressure gradient. The ablation depths of Table 1 were determined theoretically with the aid of the ablation curves [7] of each polymer. They are in good agreement experimental values which are in fact the peak-to-valley amplitude given by AFM. This is an indication that the contrast between bright and dark stripes of the image is near maximum. Only amorphous PEN shows disagreement with its theoretical estimation. The reason for this is not known.

4. DISCUSSION AND PERSPECTIVES

These experiments can be viewed as two and three "in phase" beams interference experiments. Interference experiments are classical in optics and conventional 2 beams interference laser ablation approaches have used various beam splitting elements like phase gratings [8] , splitter and mirrors [9,10], prisms , cubes [11], etc.. Our defocusing experiments (2.2) in reality uses the interference field of 3 selected beams of the mask. Less conventional and more recent multibeam (more than two) interference experiments [12] using diffracting beam splitters present some analogous features. The use of the present filtered imaging with a projection lens offers several advantages among which is the large working distance of lens to sample. It is of the order of 30 mm in our set-up, a distance which permits the use of vacuum or environmental chamber, for instance. It is interesting to note that the simple variation of the defocus distance z revealed the doubling of the lateral modulation in the ablation patterns. To our knowledge there is no literature report of this z dependence of the laser intensity in such 3 beams interference. The best example of this effect is given by PC in Fig.1a and b since its ablation is known to be "dry" *i.e.* not producing a transient liquid film like PET and PEN, that could erase the wanted pattern by flowing before solidification. Therefore PC ablation profile is sharp and predictable with simple model [6] by knowing the laser intensity profile and the ablation curve. For other polymers PET and PEN (Fig.1c-f), although transient liquid is formed and displaced during ablation [5] the spatial frequency doubling is clearly seen but the profile is strongly affected by the transient liquid effect. It is thought that this will be a main limitation for smaller grating periods. In the other type of experiment with the 2 filtered beams, we have reached smaller grating period 0.53 µm with orders ±2 selected (see Fig.2). PC is still giving a good ablation pattern with high regularity (Fig.2a). PI-Upilex which is a heat resistant polymer for high technology has also a "dry" ablation behaviour and therefore gives also a good grating pattern (Fig.2b). The other two polymers PET and PEN have ablation behaviours which depend on their crystalline morphology. They can be totally amorphous or partially crystalline like in many commercial films (Mylar, Teonex). We have observed for a long time that amorphous PET and PEN are less prone to transient liquid formation for reason of polymer solubility in the ablation products (see reference [5]). Therefore they give profiles (Fig.2c and e) not too far from the expected one that is to say with very few defects. On the contrary as in Fig.2d and f, crystalline PET and PEN display profiles strongly distorted by the transient liquid. The valleys are filled with resolidified liquid and the lines are not fully straight anymore, they show some lateral waviness. The dynamics of the transient liquid layer has been modelled in reference [5]. Because

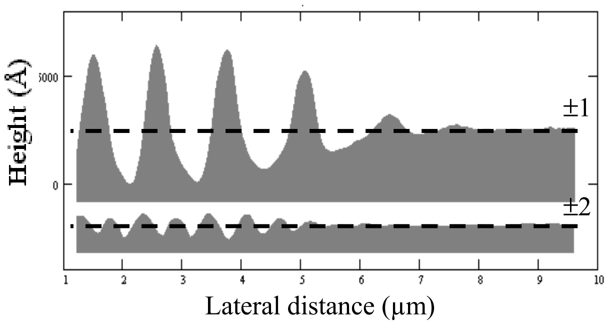

Fig.3 AFM profile of the edge of the KrF ablated patterns p=2.1 µm on PEN showing the rise of transient liquid above the original surface level (horizontal dotted line). Upper profile is for the experiments with ±1 order beams and lower one for ±2 beams.

of its low transient viscosity [13] it is accelerated by the lateral recoil pressure (several hundred bars) developed by the departure of the ablation products. This induces a lateral flow of the liquid toward the regions exposed to lower fluence.

During the timescale of one laser pulse 25 ns the flow distance is of the order of ~4 µm [5] a value close to the period of the grating image used in this work. If the pressure modulation induced by the grating ablation has a period lower than this value, then the liquid accumulates on the top of the dark stripes as in Fig.3 and its level rises above that of the original surface. This phenomenon is easily evidenced by these experiments. We can further imagine that on the top of a hill made by a dark stripe, the two incoming flows of transient liquid collide and therefore acquire some momentum in the upward direction. This is the onset of the formation of a liquid jet. In other experiment of laser fibering of the PMMA surface [14-16] we study the ejection of nanofilaments resulting of the acceleration of microdroplets in a similar way but at much higher fluence. They can be explained by a similar type of mechanism.

5. CONCLUSIONS

KrF laser ablation of polymers has been done with micron and submicron period grating-like patterned beams, created with a precision projection lens and by selective filtering of the diffracted orders of the grating mask. The two new approaches (with 2 and 3 beams) which have been developed lead to grating patterns of submicron periods as measured by AFM. New features of the ablation behaviour of polymers can be measured in these patterns, like transient liquid flow in the case where irradiation tends to melt the target or to produce liquid products. These submicron laser ablation experiments are promising for the future research development.

6. ACKNOWLEDGEMENTS

The research is partly funded by Région Aquitaine and FEDER program. Authors thank CNRS (Centre National de Recherche Scientifique) of France for a research position for VNT, who is on leave from the General Physics Institute, Moscow.

REFERENCES

[1] F.Weisbuch, S.Lazare, F.N.Goodall, D.Débarre: Appl.Phys.A **69**, (1999) S413.
[2] R.Srinivasan, B.Braren : Chem.Rev. **89**, (1989)1303.
[3] S.Lazare, V.Granier: Laser Chem. **10**, (1989) 25.
[4] F.Weisbuch, V.N.Tokarev, S.Lazare, D.Débarre : Appl.Surf.Sci. **186**, (2002) 95.
[5] F.Weisbuch, V.N.Tokarev, S.Lazare, D.Débarre: Appl.Phys.A **76**, (2003) 613.
[6] F.Weisbuch, PhD thesis, University of Bordeaux 1, (2000) n° 2178, in french
[7] S.Lazare, V.Granier: Amer.Chem.Soc.Sympos.Ser.Polym. **412**, (1989) 411.
[8] E.H.Anderson, K.Komatsu, H.I.Smith: J.Vac.Sci.Technol.B **6**, (1988) 216.
[9] R.Fedosejevs, K.J.Ilcisin: Appl.Opt. **26**, (1987) 396.
[10] P.E.Dyer, R.J.Farley,R.Giedl: Optics Comm. **129**, (1996) 98.
[11] R.Sauerbrey: Appl.Phys.Lett., **58**, (1991) 2761.
[12] T.Kondo, S.Matsuo, S.Juodakis, V.Mizeikis, H.Misawa: Appl.Phys.Lett. **82**, (2003) 2758.
[13] F.Weisbuch, V.Tokarev, S.Lazare, D.Débarre: Appl.Surf.Sci. **186,** (2002) 95.
[14] F.Weisbuch, V.N.Tokarev, S.Lazare, C.Belin, J.L.Bruneel: Appl.Phys.A **75**, (2002) 677.
[15] F.Weisbuch, V.N.Tokarev, S.Lazare, C.Belin, J.L.Bruneel: Thin Solid Films **453-454**, (2004) 394.
[16] V.N.Tokarev, S.Lazare, C.Belin, D.Débarre: Appl.Phys.A (2004) in press