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Atomic force microscopy of laser induced sub-micrometer periodic structures on implanted fused silica and silicon

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Abstract

The ultrathin layers with depth from 30 to 60 nm and optical absorption coefficient up to 10^5 cm^{-1} were created on the fused silica and crystalline silicon surfaces by Fe and Sb ions bombardment respectively. Nanometer-scale α-Fe particles formed into glass surface layer by high dose Fe^+ bombardment were responsible for optical absorption in the Fe^+ implanted fused silica. The increase in the optical absorption of Si after Sb^+ implantation are due to transformation of the silicon surface layer from the crystalline to the amorphous state. These layers were found to be easily evaporated by pulsed beam of UV and visible lasers due to their high light absorption. Such materials may be promising in manufacturing the video disk master. The sub-micrometer diffraction gratings were produced using holographic method in order to estimate the possible resolution of these media for optical data storage. It was found with Atomic Force Microscope (AFM) that microtopography of laser-induced diffraction gratings is determined by the size of optical absorption centers. After treatment with higher laser power density the half-micrometer bi-directional diffraction gratings on implanted silicon were observed by AFM. The origin of these gratings was explained in terms of the laser-induced surface electromagnetic waves.

1. Introduction

Recently atomic force microscopy (AFM) has been extensively used to investigate the interaction of laser beams with the surfaces of different materials with nanometer spatial resolution [1–4]. Two most interesting problems may be distinguished: firstly [1], the study of fundamental processes forming the basis for recording and reading of information from widely used compact disks, and secondly, the study of surface modification by laser beams, in particular, the formation of periodical micrometer and sub-micrometer structures of different nature on the surface [2–4].

In this paper we present the AFM investigation of laser induced modification of implanted fused silica (SiO_2) and silicon (Si) surfaces.

It is well known that after high dose ion bombardment the implanted near-surface layer of Si was transformed from the crystalline to the amorphous state. It results in the increase in the optical absorption coefficient from 10^2 to 10^4 cm^{-1} [5].

Not long ago we observed the increase in the optical absorption after high dose implantation of metal ions into optical glasses [6]. Optical absorption coefficient of initially non-colored glasses increased from the nearly zero value up to 10^5 cm^{-1} in the visible and UV range after implantation of Fe ions at high doses. It was conditioned by the formation of

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metal α-Fe particles with the size from 5 to 100 nm and with the average distance of about 100 nm between the nanoparticles in implanted layer after Fe^+ bombardment [6].

In these media the most part of laser pulses energy is released as heat in a thin implanted layer with a high optical absorption coefficient. This fact determines the high sensitivity of these media to light irradiation and makes them most promising for high-density optical data recording and storage.

The aim of this work was to investigate the processes on the surfaces of implanted materials under irradiation by power laser pulses. Particular attention was given to studying the influence of nanometer size of optical absorption centers on evaporation of near-surface layer under laser irradiation.

2. Experimental details

The experiments were performed with an AFM P4-SPM-MDT (MDT-Nanotechnology, Zelenograd, Russia). Vertical displacement of the sensitive cantilever in this microscope was registered by deflection of the laser beam reflected from the probe tip. The highest obtained resolution of this AFM was 0.1 nm both in a surface plane and in perpendicular direction. The sample was clamped on a tube piezoscanner that provides the scanning area of 3.7 $\times$ 3.7 μm. The constant force operating mode was realized in our experiments and the convention feedback loop circuit was used to maintain the constant force not higher then 100 nN. Automatic approach of the tip to the surface till repulsive force appeared was provided by the step driver.

Light from a low-power N_2 laser ($\lambda = 337$ nm, average output power 4 mW), operating in pulsed periodic conditions with a frequency up to 100 Hz and laser pulse duration of 10 ns was focused by a short-focus lens giving a spot size of 40 μm. Also ruby laser ($\lambda = 694$ nm, pulse duration of 10 ns) was employed for the surface modification. The experimental set-up for producing a surface modification was a traditional two-beam holographic exposure system described in [3]. The laser beam was polarized perpendicularly to the plane of incidence (s-polarization). The optical delay line was used to synchronize the instant of surface exposure by laser beams. Under a single act of simultaneous action of two coherent beams the interference pattern was formed on the surface. The lateral nonuniform heating of the surface occurred in these space periodic conditions followed by nonuniform melting, recrystallization and evaporation of near-surface layer. It resulted in keeping a 'frozen' relief-image of the pattern after the laser pulse was turned off. A higher power density was produced in the center of the light spot compared with edges due to a nonuniform (Gaussian) power distribution in the cross-section of the spot. It was shown by the topography of the obtained structures. The cross-section size of laser induced gratings was about 1 mm and it allowed one to visually observe these gratings by their characteristic glitter due to diffraction of the incident light.

Ion implantation (bombardment) of the surfaces was carried out by means of an ion accelerator ILU-3.

The Si samples were diced from n-Si (111) wafers (P-doped up to 10^{15} cm^{-3}) and implanted by Sb^+ with the beam energy of 30 keV and doses higher than the threshold of amorphization (from 10^{15} to 10^{16} ions/cm^2).

Polished plates of optical quartz glasses (fused SiO_2) were implanted by Fe^+ with the beam energy of 40 keV and nominal dose up to 4×10^{17} ions/cm^2. Preliminary surface treatment of Si and the fused SiO_2 samples included conventional rinsing in pure ethanol and deionized water.

3. Results and discussion

In our experiments, initially non-colored quartz glasses obtained a characteristic gray color after ion implantation. The optical absorption spectra and the nature of absorption centers in Fe^+ implanted fused silica were investigated and described in more detail in our earlier paper [6]. We have pointed out that α-Fe particles with the size from 5 to 100 nm were formed in glasses after high dose implantation and they were dispersed in a near-surface layer with the thickness of 60 nm. It is absorption of the light on delocalised electrons of these particles that is responsible for high values of optical absorption coefficient (up to 10^5 cm^{-1}) in the visible and UV range.

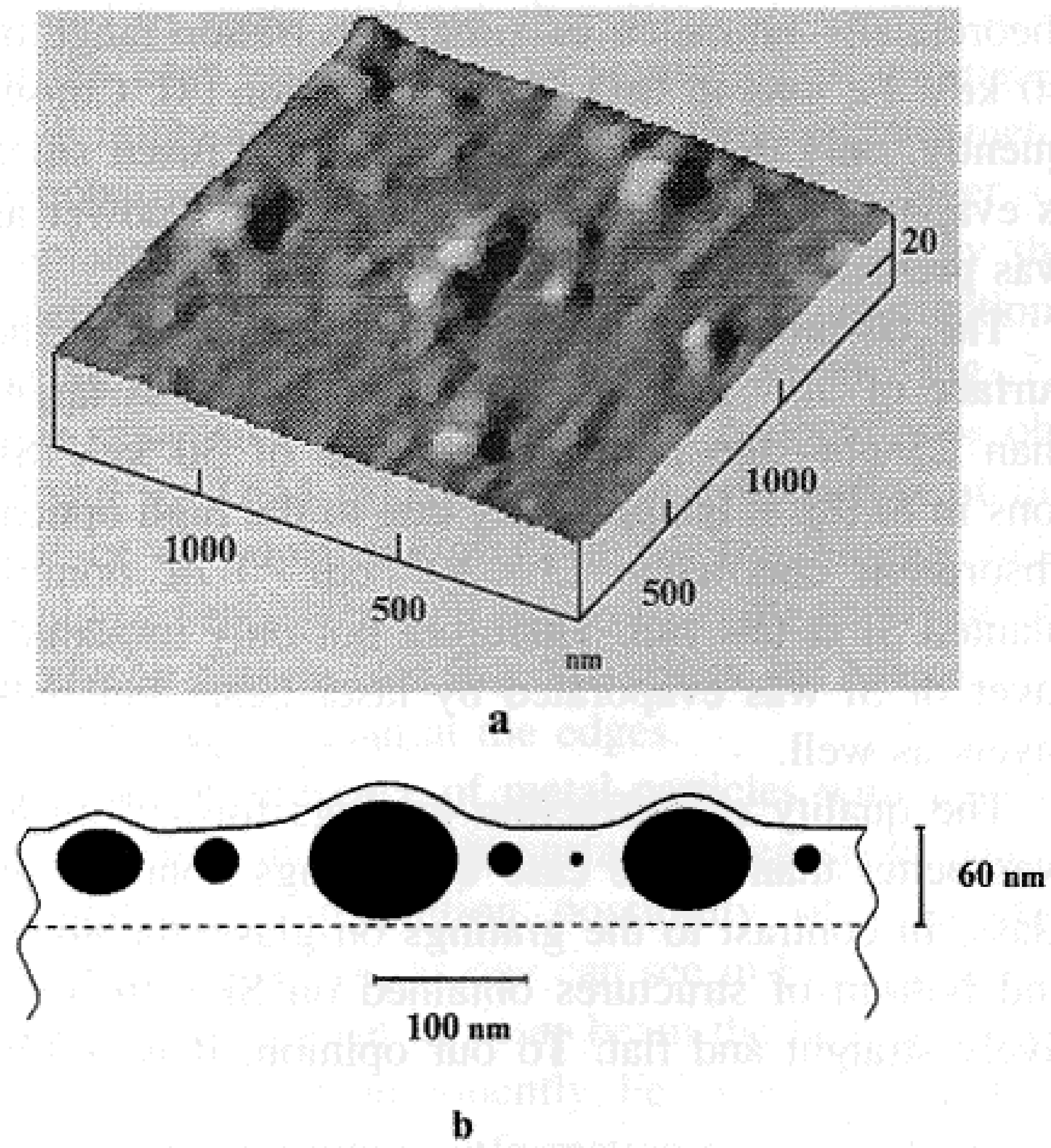

Fig. 1. Shaded AFM image of Fe^{+} implanted fused silica (a). Schematic cross-section view of implanted fused silica (b). α-Fe nanoparticles are presented by the black areas.

The typical protrusions on the surface (Fig. 1a) were observed in the AFM images of implanted glasses. Such protrusions absent in the non-implanted samples. The cross-size of protrusions and the distance between them correspond to the largest α-Fe particles which we have earlier observed in such glasses by TEM [6]. At energy of 40 keV, the Fe penetration range in fused silica did not exceed 60 nm. Therefore one can not exclude that glass forms a 'dome' above the largest α-Fe particles with size larger than 60 nm as shown in Fig. 1b. The presence of a thin protection layer of glass even above the largest particles is confirmed by experiments with chemical etching of the surfaces of such prepared glasses. The treatment by 2% aqueous solution of H_2SO_4 did not lead to a detectable decrease in the optical absorption coefficient, whereas the etching of the 60 nm implanted layer in 0.1% aqueous HF solution resulted in complete discoloring of implanted glasses.

It is extremely important that almost all incident light was absorbed in a very thin implanted layer. Therefore it was possible to make a desired picture on the surface by a pulsed beam of the N_2 laser focused into the spot with a diameter of 40 μm. Our calculations showed that the laser power of 4×10^7 W/cm^2 is high enough to cause the evaporation of the layer of glass colored by implantation. It was the same power of the laser pulse that was obtained on glass surface under illumination by N_2 laser beam focused down to 40 μm. It was possible to produce lines and dots with desired configuration through moving the sample relative to the laser beam due to the evaporation of near-surface implanted layer. Lines with the width of 40 μm and dots with diameter of 40 μm were easily observable through optic transmission microscope due to essential enlightenment of the glasses in the places of evaporation of implanted layer.

Local modification of absorption and reflection coefficients under the evaporation at a given depth provides a basis for optical recording of binary information on the compact disks using a laser beam focused to 0.8–1 μm. Our previous investigation shows high mechanical resistivity of the metal films formed under ion implantation because these films are buried in a near-surface layer of the glass. It makes these films most promising for high-density recording and storage of optical data. However, the resolution of such medium has not yet been clear enough because of finite sizes of randomly spaced absorption centers that could considerably reduce the resolution.

In practice, it is difficult to focus the laser beam into a spot with a diameter less than 1 μm. Therefore in order to estimate the evaporation depth and possible resolution of implanted glass medium we have applied the method of the formation of holographic diffraction gratings with the spatial period of 0.9 μm by means of a pulsed beam of a ruby laser [7]. In this case the local evaporation occurred in the locations of the interference maxima that were produced by two crossed laser beams.

For comparison the diffraction gratings formed in this way on the amorphous silicon surface are used in our experiments. An amorphous surface layer of Si induced by Sb^{+} implantation has predominantly the Ångström-scale centers of light absorption [5] in contrast to Fe^{+} implanted fused SiO_2 containing the nanometer-scale absorption centers (α-Fe nanoparticles). Therefore a near-surface layer of amorphous Si must absorb the incident light more uniformly and

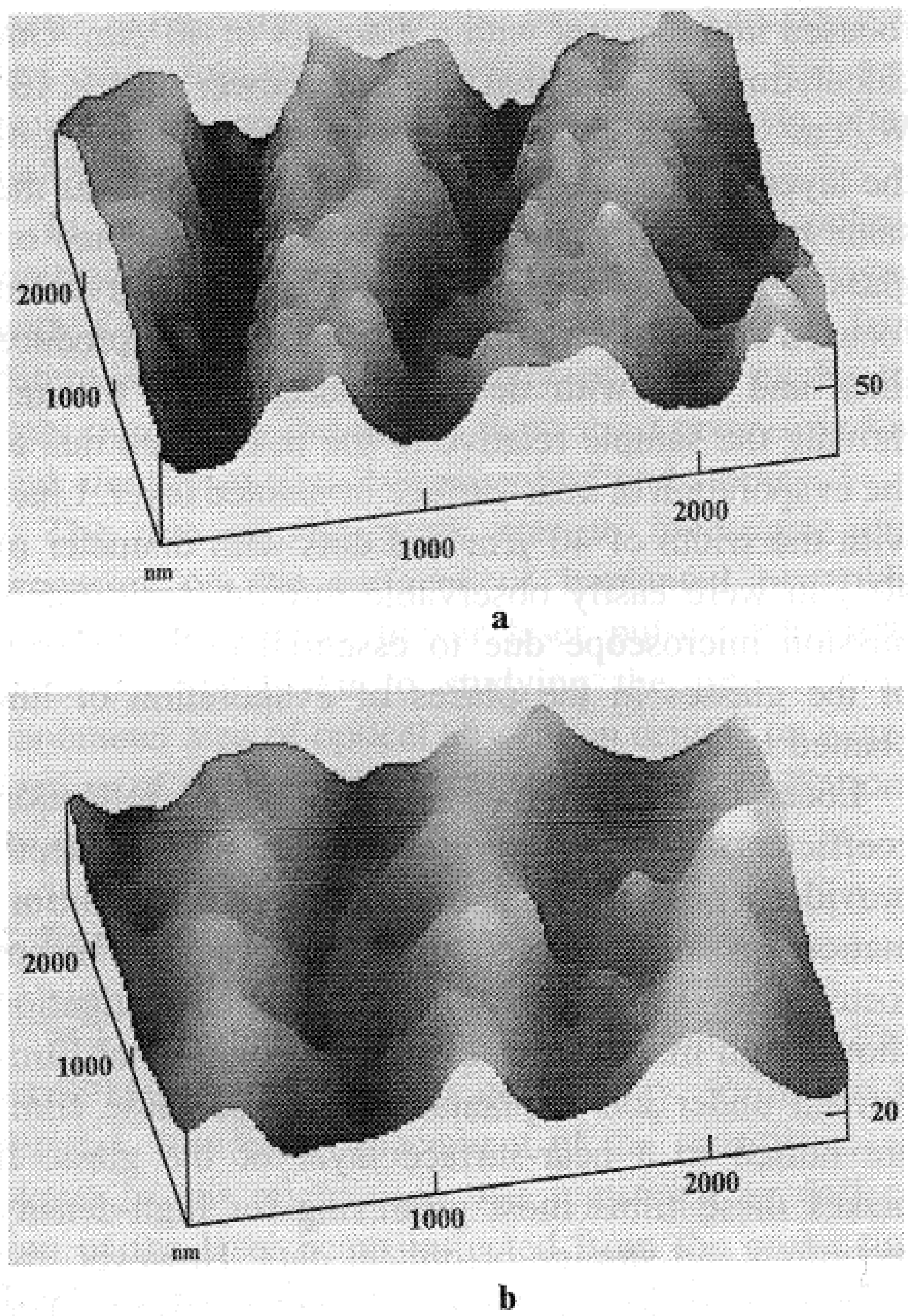

Fig. 2. AFM images of laser induced diffraction gratings obtained on the Fe^+ implanted fused silica at low (a) and high (b) laser power density.

show a higher optical resolution for the holographic storage. The diffraction gratings formed on implanted Si surfaces by laser beams were investigated with Scanning Tunneling Microscope (STM) in our previous work [7].

Fig. 2 presents the AFM images of diffraction gratings formed using a holographic method on the surfaces of implanted fused silica. AFM images are presented as a combination of relief and gray-scale shadowing. The spatial period of observed gratings $d = 0.9$ μm is in good agreement with that determined using a well-known expression $d = \lambda/[2\sin(\alpha/2)]$ with λ the wavelength of the incident laser radiation, α the angle between the interfering laser beams [7].

The depth of the laser induced holographic grating was 70 nm. This value is close to 60 nm – the theoretically estimated maximal penetration range of 40 keV Fe ions in SiO_2 at implantation [8]. Consequently, only the implanted layer of the fused silica is evaporated under used densities of laser power as was presumed above.

The 60 nm depth of the grating obtained on the surface of Sb^+ implanted Si (see Fig. 3a) is larger than 25 nm – the penetration range of 30 keV Sb ions in Si [8]. It is apparently due to the high optical absorption coefficient (3×10^3 cm^{-1}) of nonimplanted Si at 694 nm. Therefore not only implanted layer of Si was evaporated by laser beam but bulk layers as well.

The quality of diffraction gratings formed on Si was better than in the case of gratings obtained on glass. In contrast to the gratings on glass, the edges and bottom of structures obtained on Si were relatively straight and flat. To our opinion, it is condi-

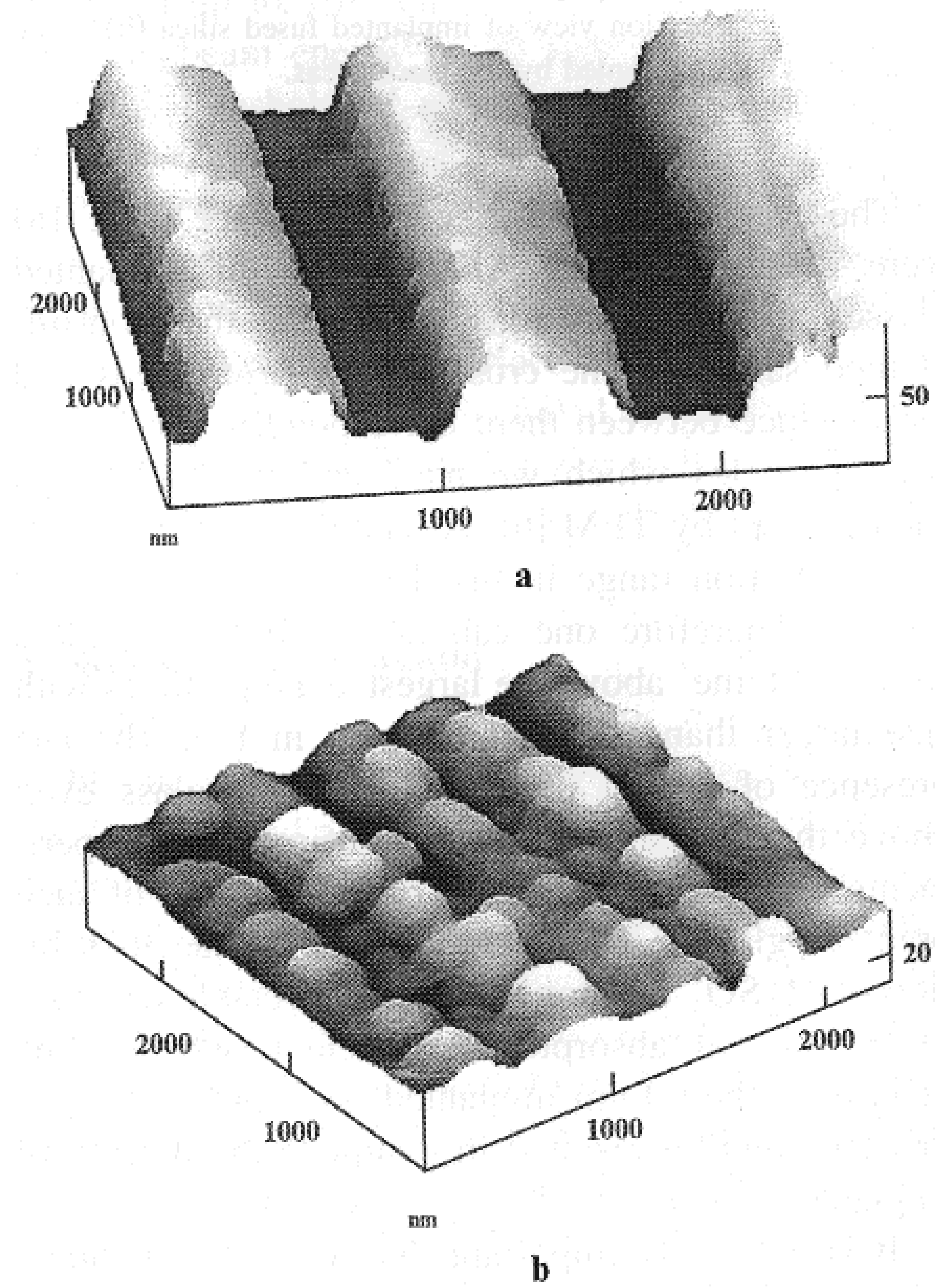

Fig. 3. AFM images of laser induced diffraction gratings, obtained on the Sb^+ implanted silicon at low (a) and high (b) laser power density.

tioned by more uniform absorption of incident light in the near-surface layer of implanted Si compared with implanted layer of the glass that contains metal nanoparticles. Therefore the near-surface layer of implanted Si is more uniformly evaporated by the laser beam. The size of typical surface imperfections on the glass gratings is about 50–100 nm (Fig. 2). The same size had the largest Fe nanoparticles observed by TEM [6]. Nonuniform evaporation of the surface of implanted glass in the interference field could be especially well observed in the center of the produced grating (see Fig. 2b) where the laser intensity was higher than at the edges.

Thus the presence of metal particles with size up to 100 nm in the near-surface layer significantly decreased the resolution possibility of implanted glass. Nevertheless, as one can see in Fig. 1a, it was possible to produce by laser beam the lines with the size of 0.4 μm. Consequently, Fe^+ implanted glasses are suitable for binary information recording with the density of 10^7 bit/cm^2.

Two-dimensional dot-structures were observed in the central part of some holographic gratings on Si surfaces, where the laser intensity was maximum (see Fig. 3b). The spatial period of these new dot-structures in the direction of periodical changes in the profile of above discussed one-dimensional gratings was about 0.5 μm. Simultaneously, the regular surface structure with the period of about 0.4 μm was observed in the perpendicular direction coinciding with the direction of the s-polarized laser electric field.

The formation of additional regular surface structures in the direction coinciding with the direction of the polarization of the incident laser beam and with the spatial period of about the wavelength of incident light is usually attributed to the interference of incident laser wave and the wave scattered initially by surface roughness and afterwards by holographic grating and propagating in the surface plane [9]. As a result, modulation of optical intensity appears with a spatial period $d \approx \lambda$ in the direction coinciding with the direction of the laser electric field, i.e. perpendicular to the corrugations of the holographic grating. Akhmanov et al. consider that periodical structures with $d \approx \lambda$ arise due to interference between the incident laser light and surface electromagnetic waves (SEW) [9]. In this case, SEW are excited through scattering of incident laser light on the nonuniformities of semiconductor melt. It is typical to metal surfaces but it was suggested that semiconductor near-surface layer becomes metal-like under melting by laser beam.

This model is also employed in order to explain of the formation of ripple structures with $d \approx \lambda/n$ (where n is the refractive index of the material) oriented parallel to the electric field of incident light. Modulation of optical intensity with the period less than λ results from the interference of incident laser light with the light mode excited in the asymmetric gradient surface waveguide produced by the increase in the refractive index under semiconductor heating by the incident laser irradiation.

In principle, simultaneous generation of SEW and light wave in surface waveguide can occur under strong heating and metallization of semiconductor near-surface layer [10]. Thus two-dimensional optical interference field appears in near-surface semiconductor layer.

These effects could apparently explain the formation of surface structures shown in Fig. 3b with the period making approximately one half of the wavelength of the incident laser light. However one can not exclude that regular structures observed by AFM are the interference of the waves on the surface of the semiconductor melt (capillary waves) excited during the laser pulse. Further AFM investigations with high spatial resolution of the gratings formed by pulsed laser irradiation may produce additional information about the nature of these objects.

4. Conclusions

We have demonstrated the successful employment of AFM for the investigation of periodical interference structures induced by pulsed laser beams on glass and semiconductor surfaces. High spatial resolution AFM allows one to investigate fine details of the interaction between incident light and the surface, in particular, the influence of the sizes of light absorption centers on the formation of the surface microrelief under local evaporation by the laser beam.

It was shown that evaporation of the implanted layer of fused silica occurs nonuniformly because of the presence of optical absorption centers with cross-section up to 100 nm. The surface imperfections after evaporation had the same size as α-Fe nanoparticles buried into the implanted layer. Nevertheless one can produce the sub-micrometer diffraction gratings on the surface of these media using laser beams that enables using of implanted glasses to produce compact disk master.

The half-micrometer bi-directional diffraction gratings with periods making approximately one half of the period of conventional holographic diffraction gratings were formed by laser beams on the surface of implanted Si. These two-dimensional structures with the period considerably less than the wavelength of incident laser light are due to the interference of the incident light wave with electromagnetic waves propagating along the implanted layer and excited by incident laser light.

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