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Modification of optical properties and structure of thin films for enhancing absorption

V.O. Lysiuk
V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine
41, prospect Nauky, 03028 Kyiv, Ukraine
E-mail: lysiuk@univ.kiev.ua

Abstract. The most used methods such as ion implantation, laser irradiation and nanosphere lithography for modification and creation of special microrelief of thin absorbing films on photosensitive substrates have been described. Controlled modification of surface structure of the samples for improving their optical properties, especially for enhancing absorption, has many applications in optical devices. The basic things were analyzed from selection of film materials and ways for their further processing to shapes and dimensions of the obtained surface structures. Theoretical modeling methods based on the Mie theory and statistical temporal mode-coupled theory have been used to explain the influence of surface microrelief on optical properties of the samples. Advantages and perspectives for application of the methods have been described and analyzed.

Keywords: thin films, light trapping, absorption coatings, surface structure.

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1. Introduction

Deposition of thin absorbing films plays a basic role for transformation of light energy to its other kinds for sensing elements of photodetectors, sensors, solar cells and other systems. Optical properties of thin films should satisfy requirements on transmission and absorption bands, reflection and refraction coefficients and adhesion of these films to the substrate. So, selection of the absorbing material, method of its deposition and further processing are the basic steps of sample preparation.

To enhance absorption of thin films, the critical requirement is the relation of dimensions of the structures a with the light wavelength λ. Thus, at $a << \lambda$ the polar scattering diagrams are symmetrical. So, the intensity of light scattering is maximal and is the same in direction of forward and back and is minimal in the symmetry plane. Increasing a, the intensity of forward scattering is higher than that for back scattering (Mie effect) [1]. At $a >> \lambda$, the highest intensity of light scattering will be for the back one. It can be simply explained as shown in Fig. 1 and table [2]. So, for increasing absorption of thin films or surfaces of the samples, the dimensions of structures should be of the order of the wavelength. To fulfill this requirement, it is necessary to make appropriate processing of the surface.

It can be used one of the proposed methods for surface modification: ion implantation, laser irradiation and nanosphere lithography, etc. But the most effective method for different individual case should be specific, and its applicability should be analyzed.

2. Overview of methods

Ion implantation causes disposition of atoms in solid from their stationary locations. These atoms having enough kinetic energy became secondary bombardment particles and cause appropriate dispositions of other atoms in the lattice. As a result, a cascade of disposition of atoms can be formed. On its free path, the implanted ion may cause a lot of such cascades in the volume surrounding its track [3]. These avalanche processes cause radiation defects in the lattice and lead to appearance of an amorphous area and destroy the long-range order in crystals [4]. In separate cases, ion implantation can lead even to phase transformations, which depends on material composition, energy and dose of implanted ions. Mechanism of blisters formation consists in deformation of subsurface layers of film under the pressure of inert gases that was implanted as ions into the sample. The coefficient of surface tension of the materials is decreased when necessary doses of implantation are reached, which increases the probability of blisters formation on the surface of sample. By selecting material composition, type, energy and dose of implantation as well as the temperature of materials and that of further thermal annealing, it is possible to reach large-scale blisters formation (Fig. 2) that will effectively increase optical absorption of the sample for various applications [5].

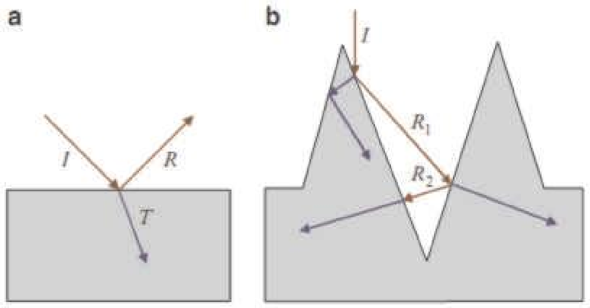

Fig. 1. (a) Light specularly reflecting from a flat surface. (b) Multiple reflections from protruding structures enhance coupling into the material, and refraction causes the light to prorogate at oblique angles, increasing the optical path length [2].

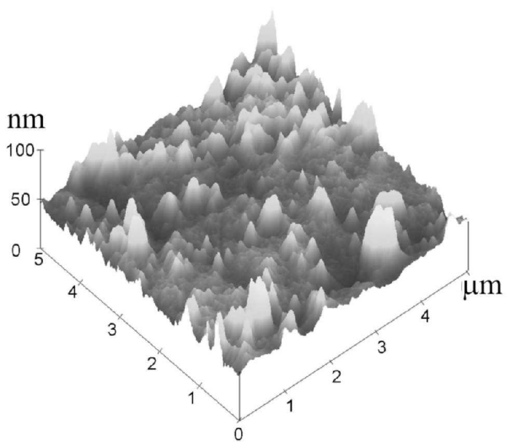

Fig. 2. Typical microrelief of thin Ni films on lithium niobate implanted by Ar^+ ions with the energies of 100 keV [5].

Table. Multiple length scales over which reflectivity and absorption is determined by surface features.

Feature size	Influence on reflectivity
$a >> \lambda$	Light trapping due to multiple reflections enhances coupling into the material. Light refracted at oblique angles increases the effective optical path length
$a \approx \lambda$	Small features can successively scatter light, increasing the effective optical path length and enhancing absorption
$a << \lambda$	Subwavelength structures (SWS) can reduce reflections through the moth-eye effect

Laser irradiation along with ion implantation is one of new effective methods to modify the surface structure. One can use a pulsed power or CW laser with the system of scanning laser beam on the surface of the sample. Similar to the previous case, interaction of laser irradiation with solids is accompanied by effects of atom intermixing, hardening and generation of defects. But the dominant mechanism of intermixing by laser irradiation is diffusion in liquid phase, which takes the time when the surface is in the melted state. This is also related to systems metal-semiconductor. The diffusion in liquid phase takes time 10^5 less than that in the solid phase [6]. According to calculations, the radiation energy of applied laser melts solid to the maximal depth in its case. Then, with transferring the heat from the surface melt to the substrate bulk, the front of melting moves in the same direction. Estimation of the time when the sub-surface layer is kept in the state of the melt enables to determine the rate of hardening of the solid in the terms of temperature changes: $10^9 \ldots 10^{10}$ K/s, sometimes up to 10^{14} K/s when using the UV lasers with shorter pulses. The typical structure of the surface as an example of Si processed by 800 nm 100 fs pulsed laser (10 kJ/m^2) is shown in Fig. 3 [2]. Application of laser pulses to modify properties of sub-surface layers and structure of material surfaces can be successfully used to create structured surfaces as well as to improve absorbing properties of the samples.

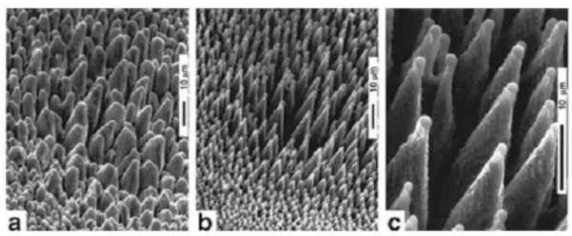

Fig. 3. SEM images of the surface microstructuring of Si(100) by 500 laser pulses of the 200-mm diameter, nearly Gaussian beam (100 fs, 800 nm, 10 kJ/m^2) (*a*) processed in vacuum and (*b*,*c*) in the 500-Torr atmosphere of SF_6. Images viewed at the angle 45º from the surface normal [2].

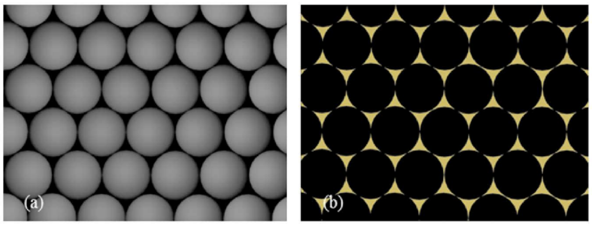

Fig. 4. Illustration of the nanosphere lithography fabrication method. (a) Render of the hexahonal close-packed monolayer that is used as a deposition mask, and (b) render of the nanoparticle array that results after metal deposition and removal of the microsphere mask [7, 8].

Nanosphere lithography is the newest method to fabricate microstructures. Despite primary application of this method with localized surface plasmon resonance (LSPR), it can be successfully applied for coating surfaces with ordered micro- and nanostructures of required geometry for various applications. Nanosphere lithography has been used to produce inexpensive nanoparticle arrays, through the use of monolayers of self-assembled microspheres as a deposition mask. However, lack of control over the location and size of the arrays, as well as poor uniformity over large areas, limit its use to research purposes. There are two prospective methods for large-area fabrication of nanoparticle arrays: convective self-assembly nanosphere lithography and geometrically confined nanosphere lithography. In geometrically confined nanosphere lithography method, microsphere assembly is confined to geometric patterns defined in photoresist. It was shown in the paper [7, 8] that 400-nm polystyrene microspheres can be assembled inside of large arrays of photoresist trenches from 4…20 μm in width and 500 μm in length, with high uniformity, repeatability and quality. Compared to convective self-assembly nanosphere lithography, geometrically confined nanosphere lithography allows precise patterning of nanoparticle arrays for use in practical sensing devices, while still remaining inexpensive. The typical structure of the surface fabricated by nanosphere lithography method is shown in Fig. 4 [8].

More precise methods such as electron-beam lithography and plasma etching offer higher resolution, uniformity and repeatability for microstructures array fabrication, but it is not economical, especially in comparison with nanosphere lithography.

3. Results and discussion

In general, micro- and nanostructures fabrication approaches can be divided into two methods: deposition (bottom up) and etching (top down) ones [9]. It is well known that the light absorption of a bulk material is limited by the Yablonovitch limit [10], which sets an upper limit to the amount of electromagnetic intensity that can be trapped in material. The standard theory of light trapping demonstrated that absorption enhancement in a medium cannot exceed a factor of $4n^2/\sin^2\theta$, where n is the refractive index of the active layer, and θ is the angle of the emission cone in the medium surrounding the cell. Recent theoretical developments showed that this limit can be overcome by using nanophotonic strategies, which can improve light trapping and thus, light absorption by order of magnitudes. Yu et al. [11] proposed a statistical temporal mode-coupled theory to describe the trapping enhancement in periodic photonic nanostructures. This theory reveals that the conventional limit can be substantially surpassed when optical modes exhibit deep-subwavelength-scale field confinement, opening new avenues for highly efficient next-generation sensing systems.

In the paper [12], the authors proposed a new approach, in which the waveguide nature of thin films is combined with a random distribution of nanoscale holes to improve the light coupling to the Si slab. Light impinging from the vertical direction couples to the modes generated by the 2D multiple scattering. The absorption is independent from polarisation and is broadband. The structures were simulated using the 3D finite-difference time-domain method. The dispersion of the samples was modeled by fitting tabulated data with Drude-Lorentz expression. Results from calculations and measurements on the absorption of the Si bare slab and the Si perforated (ion beam lithography and plasma etching) slab are compared. A clear enhancement of absorption is obtained for both polarizations and at all wavelengths. The measurements and simulations are quantitatively in very good agreement. The intensity of the trapped light in the random structures is clearly enhanced as compared with that in the bare slab. These samples can be applied in solar cell technology for increasing energy transfer coefficient.

In the papers [5, 13-14], the authors compared absorption of deposited thin Ni, Mo and Pd films on lithium niobate with the same samples implanted by Ar^+ ions. As shown in AFM and SEM images, the surface of implanted samples was covered by blisters. Absorption of implanted Pd film on lithium niobate was enhanced up to 80% in the wide spectral range (λ = 1…15 μm). These systems are used in pyroelectric photodetectors and power meters, so enhancing absorption will benefit sensitivity, but atom intermixing process at the interface film-substrate increases adhesion of the film to substrate and, respectively, damage threshold.

In first and second cases, we can observe enhancement of absorption in different materials by modification of their surface structure. The fabricated by deposition or etching micro- or nanostructures may outperform existing results with the light absorption exceeding 80%.

4. Conclusions

The used methods such as ion implantation, laser irradiation and nanosphere lithography for creation special surface structure of the absorbing films increasing their absorption and decreasing reflection have been described. The Mie theory and statistical temporal mode-coupled theory have been used to describe mechanism and to find key parameters (shapes, dimensions and ordering of surface micro- and nanostructures) for efficient enhancing absorption. The overviewed methods of surface structure modification have variety of applications including photovoltaics, infrared sensing, optoelectronics etc.

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