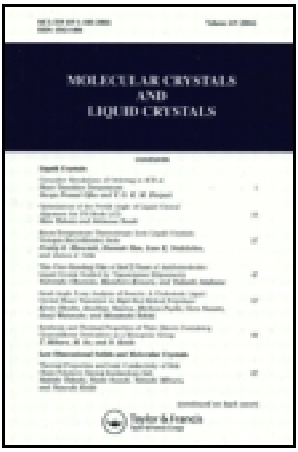

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Orientation of Liquid Crystalline Molecules on Mid-IR Transparent Plates Subjected to Ion Bombardment

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Optical absorption of the nematic liquid crystal 4-methoxybenzilidene-4′-butylaniline (MBBA) was examined to study a possibility of homogenous orientation of liquid crystalline (LC) molecules on the silicon and germanium substrates subjected to argon ion bombardment. The integral absorption near the 1630 cm^{-1} *absorption band maximum, commonly assigned to the group -CH=N- vibrating along the MBBA long axis was analyzed before and after the application of the electric field above the threshold voltage of the Fredericksz effect. It was shown that upon increasing ion fluences, the preliminary bombardment of the substrates by argon ions with energies of 250 eV lead to the planar molecule orientation. Argon ions of 1.25 keV, however, promote planar orientation only until fluences of the order of* $1 \cdot 10^{18}$ *ion* $\cdot$ cm^{-2} *and change the orientation for homeotropic at higher fluences.*

Keywords Germanium; infrared absorption; ion bombardment; ion fluence; liquid crystal; silicon

1. Introduction

In order to observe an appreciable electro-optic effect in a liquid crystal (LC), it is absolutely necessary to preliminary orient the LC molecules on the cell surfaces. Then molecules of subsequent layers are aligned to molecules of the surface layer and the whole volume will act as a single crystal. However, the well-known methods [1] for homogeneous orientation of LC molecules are not always applicable. For example, the preparation of the photon crystals with LC stuffing [2] imperatively requires refraining from rubbing. Besides, often used surfactants are undesirable if LC is purposed for special problems of the infrared (IR) light filtration [3]. Therefore, the search for alternative methods of surface processing is an actual problem. One of such methods is considered to be surface bombardment by ions of neutral gases.

Atoms can be volatilized from the surface upon bombardment by ions. This process is called sputtering. Surface erosion due to sputtering leads to changes in the

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Address correspondence to T. D. Ibragimov, Institute of Physics of National Academy of Science, 33 H.Javid Avenue, AZ1143, Baku, Azerbaijan. Tel.: +994-12-4310992; Fax: +994-12-4310992; E-mail: tdibragimov@mail.ru structure of surface layers and is characterized by a sputtering yield that is defined as the average number of atoms released from the surface of a solid by one particle. Sputtering yield depends on the energy of the ions, their mass, incident angle, mass of target atoms, target crystallinity, and the surface binding energy of the target material. Below a certain threshold energy, which for normal incidence of ions is 20–40 eV, there is practically no sputtering. Above the threshold, the sputtering yield increases with increasing energy of the incident ion and reaches a broad maximum in the range 5–50 keV [4]. A decrease of sputtering yield at higher energies is due to an increase in the penetration depth of the primary ions into the target and a decrease in the fraction of energy transferred by them to the surface layers. Sputtering of the surface by accelerated ions of sufficient energy and fluence form microscopic hollows that can act as orientation centers for elongated LC molecules.

The present work reports the observation of the orientation of LC molecules with preliminary argon ion bombardment of the Si and Ge substrates transparent in mid-IR spectral region.

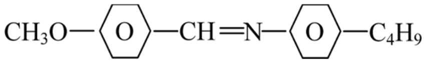
2. Experimental Methods

Setup was assembled on the base of the VU-1 sputtering plant for bombardment of plate surfaces by argon ions. High-purity p-type silicon and germanium plates transparent in the mid-IR region were bombarded by argon ions with the fluence determined by exposition time.

A pair of plates was fixed on the metal plain base and was then suspended above the high-voltage electrode. High-purity argon was used as the working gas. A glow discharge was ignited in the chamber by supplying the voltage to the electrode. Processing regime parameters were the following: ion energy of 250 eV, ion current density of 0.2 mA/cm^2, and working gas pressure of 10 Pa. The ion fluence (D) was determined using expression $D = j\ t/e$, where j – ion current density, t – exposition time, e – ion charge.

Necessary for more effective surface treatment, the argon ions with increased energy were obtained using a source of Kaufman type [4]. In order to reach dense plasma regime, the discharge with the heated cathode was used in a longitudinal magnetic field. Owing to the electron oscillations in transverse electromagnetic fields, high to uniformity plasma was developed. The parameters of the used source were as follows: cathode heating current-12 A; magnet coil current-up to 30 A; discharge current-up to 2 A; discharge voltage-up to 100 V; energy of ions-up to 2 keV; ion beam current-up to 30 mA; ion current density-up to 100 μA/cm^2. The accelerated ions were directed perpendicularly to the plate surface at both methods.

Nematic LC 4-methoxybenzilidene-4′-butylaniline (MBBA) was examined to check orientation of the molecules. MBBA has negative dielectric anisotropy and is described by the structural formula



The study of the LC molecule orientation was carried out in so-called "sandwich" cell that consisted of two identically processed silicon or germanium parallel plates between which the liquid crystal MBBA was placed. The treated surfaces of the plates were in contact with the LC. The LC layer thickness was controlled by Teflon gasket and was 10 µm. The cells were filled with LC in the isotropic phase. The direct voltage was applied to the cell.

IR absorption study was carried out on a double-beam infrared spectrophotometer Specord-75 IR in the frequency region 4000–400 cm^{-1} at room temperature. Nonpolarized light fell perpendicularly to the cell surface. The resolution and an accuracy of the frequency determination were better than 2 cm^{-1}.

3. Results and Discussion

The novel concept of monitoring the orientation of LC molecules by IR spectroscopy assumes that the maximum absorption is obtained if the electric vector of the incident light coincides with the corresponding vibration along the long axis of the LC molecule. If the direction of the electric vector of the incident radiation is perpendicular to that of the vibrations along the long axis of the molecule, then the corresponding band will have the minimum intensity. All molecules are arranged along the cell plane and the corresponding band has the maximum intensity with application of a direct voltage above the Fredericksz threshold to the cell with LC of a negative dielectric anisotropy.

For orientation control of the elongated MBBA molecules we used the absorption band with the maximum at 1630 cm^{-1}, which corresponds to the -CH=N- group vibrating along the long axis of the molecule [5]. The transmission spectrum in the spectral range comprising this band is shown in Figure 1. Preliminary use of linearly polarized radiation showed that the polarization direction did not affect the band intensity.

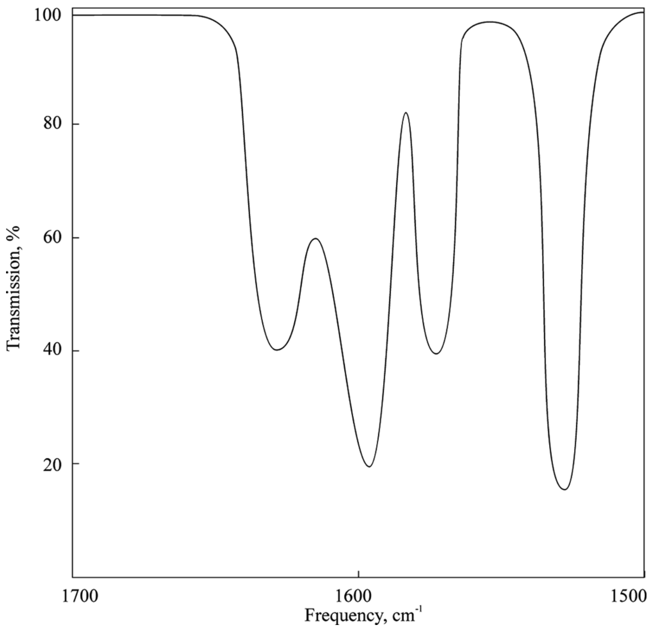


Figure 1. Transmission spectrum of the untreated silicon cell with MBBA (thickness of 10 µm) near the band corresponding to vibration of the group -CH=N-.

Careful examination showed that only 1630 cm^{-1}-band maxima displays voltage dependence of the absorption intensity. The other bands in Figure 1 remain practically unchanged with increasing the voltage applied to the cell. All this is illustrated by Figure 2. As seen from this Figure, the intensity of the light passing through the cell at 1630 cm^{-1} gradually decreases with increasing the voltage above 3.6 V and this decrease is saturated at 7.0 V. Farther voltage elevation brings the intensity back to higher values. The onset of the increase of the absorption at 1630 cm^{-1} is indicative of the turning and reorientation of the LC molecules under the applied field. Saturation corresponds to the coincidence between the vibration direction of the group -CH=N- and that of the electric vector of the incident radiation. In the last case, the LC molecules are overwhelmingly oriented in the plane parallel to the substrate surface and only the turbulence (electrohydrodynamic instability) triggered by voltage increase above 7.0 V and commonly encountered in liquid crystals with negative dielectric anisotropy, breaks the situation back to reversal, as it is observed in Figure 2.

The integrated absorption of a resonance band is known to be proportional to the number of oscillators corresponding to this optical transition. Calculations showed that the integrated absorptions of the band with a maximum at 1630 cm^{-1} without and with application of voltage of 7.0 V were $16.1 \cdot 10^5$ ion $\cdot$ cm^{-2} and $19.2 \cdot 10^5$ ion $\cdot$ cm^{-2}, respectively. The first value corresponded to non-orientated LC molecules; the second, to their fully planar orientation. The orientation of the LC molecules after bombardment of the substrates can be judged from the integrated absorption without an applied field whereas the integrated absorption at 7.0 V coincided for all types of substrate surface bombardment. If the integrated absorption after substrate bombardment was greater than $16.1 \cdot 10^5$ ion $\cdot$ cm^{-2}, corresponding to a cell with untreated substrates, then the molecules preferred to be planar; if less than this value, they were homeotropic. The deviation corresponded to the degree of one orientation of the molecules or another.

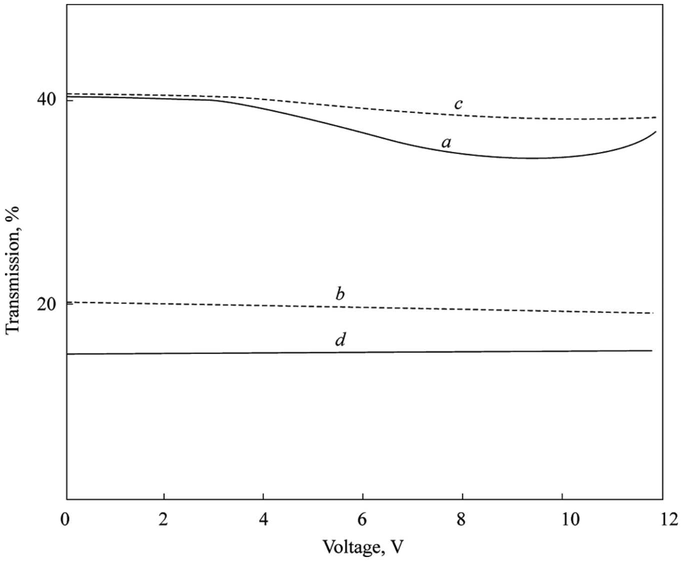


Figure 2. Light transmission of the untreated silicon cell with MBBA as a function of applied voltage at various frequencies: a – 1630 cm^{-1}; b – 1596 cm^{-1}; c – 1575 cm^{-1}; d – 1512 cm^{-1}.

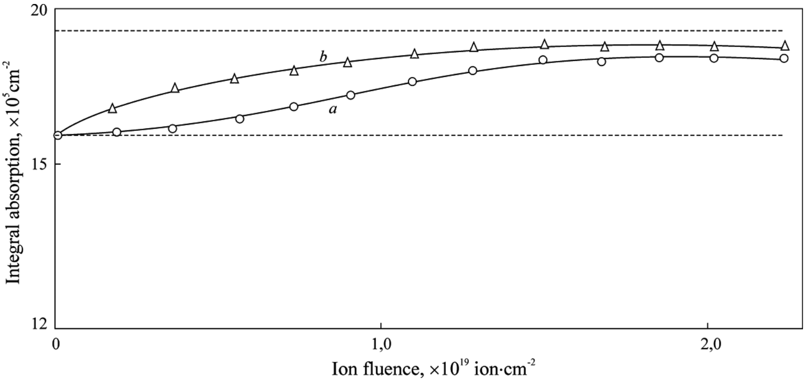


Figure 3. Integrated absorption of the band with maximum at 1630 cm^{-1} corresponding to –CH=N– group vibration as a function of ion fluence after bombarding the silicon (a) and germanium (b) substrates by argon ions with energy of 250 eV.

Figure 3 displays the ion fluence dependence of the 1630 cm^{-1}-band integrated absorption at preliminary bombardment of silicon (a) and germanium (b) substrates by argon ions with energy of 250 eV. As seen from this Figure, in both cases the LC molecules tend to assume planar orientation with increasing fluence. At the same time, in compliance with the fact that sputtering yield for germanium is larger than for silicon, such orientation is attained on germanium substrates at less ion fluences.

At low fluences, argon ions with energy of 1.25 keV also promote planar orientation of LC molecules (Fig. 4, fluencies below $1.1 \cdot 10^{18}$ $ion \cdot cm^{-2}$ and $0.8 \cdot 10^{18}$ $ion \cdot cm^{-2}$ for Si and Ge, respectively). However, at higher fluences the reverse effect with homeotropic orientation of LC molecules is observed (Fig. 4, fluencies above $1.1 \cdot 10^{18}$ $ion \cdot cm^{-2}$ and $0.8 \cdot 10^{18}$ $ion \cdot cm^{-2}$ for Si and Ge, respectively). Note that homeotropic orientation is observed in germanium plates at less fluences, which again seems to be due to larger sputtering yield for germanium.

Two opposing effects arose with bombardment of crystals by ions of different fluences. A surface initially somewhat corrugated became smooth at low fluences

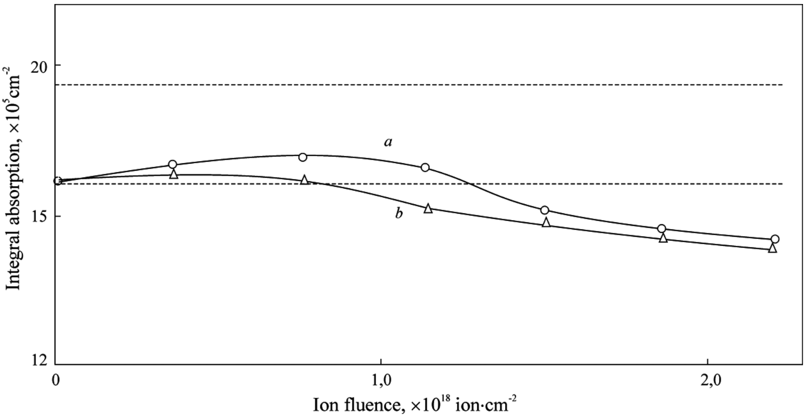


Figure 4. Integrated absorption of the band with maximum at 1630 cm^{-1} corresponding to –CH=N– group vibration as a function of ion fluence after bombarding the silicon (a) and germanium (b) substrates by argon ions with energy of 1.25 keV.

[6]. A rather large number of radiation defects accumulated within the crystal at higher fluences and led to the development of surface relief. The surface bond energy decreased and the sputtering yield increased near the defects because of the presence of mechanical stresses. The initial surface roughness could be increased for a poorly prepared surface. In this instance, crests, cones, canals, and pits developed. Such structures did not differ greatly from those that appeared on samples that were initially well polished. The surface irregularities increased with increasing ion fluence. Some portions were sputtered faster than others due to defects of the crystal lattice. Etching pits that were the most characteristic types of depressions resulting from sputtering were formed. They arose as the result of selective sputtering of emergence sites of screw dislocations onto the surface. Pits were formed in local surface regions where some dislocations or others occurred and the atomic bond energy was reduced. This increased the sputtering. The number of pits grew with increasing ion fluence. They overlapped and increased in size. Obviously, pit formation predominated with bombarding ions of energy 1.25 keV. These were centers of homeotropic orientation of LC molecules at sufficiently high ion fluences.

4. Conclusions and Perspectives

We have performed a comparative study of the effect of the argon ion bombardment on orientation of LC molecules on the Si and Ge substrates transparent in mid-IR region. It was shown that the preliminary bombardment of the Si and Ge substrates by argon ions with energy of 250 eV promotes planar orientation of LC molecules and the effect increases with increasing ion fluence up to $2.2 \cdot 10^{18}$ $\text{ion} \cdot \text{cm}^{-2}$. On the other hand, the planar orientation of the LC molecules is changed for homeotropic at fluences of the order of $1 \cdot 10^{18}$ $\text{ion} \cdot \text{cm}^{-2}$ if the argon ion energy is as high as 1.25 keV. This research provided a basis for an alternate technology for known methods of LC molecule orientation and could be widely applied for preparing infrared devices based on LC.

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