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OPTICAL SPECTROSCOPY of GaS NANOPARTICLES

FORMED via LASER ABLATION

A.M. Pashayev¹, K.R. Allahverdiyev¹, E.Y. Salayev², B.H. Tagiyev^{1,2}

¹National Aviation Academy of Azerbaijan ²Azerbaijan National Academy of Sciences, Institute of Physics

kerim.allahverdi@gmail.com

Bulk single crystals of GaS were grown by Bridgman method. Nanoparticles of quasi 2-D GaS crystals were obtained by laser ablation technique and characterized by: NXRF; NGDOES; NSEM and TEM; NUV-VIS absorption. Nanoparticles were ablated by using the line $\} = 248$ nm of excimer KrF laser operated at f = 50 Hz with pulse duration $\ddagger = 4$ ns and maximum energy 200 mJ. Obtained results are analyzed with respect to particle size. Absorption spectra of particles with diameter less than 18 nm turned out to be shifted in the blue range of spectra. This result is consisted with a weak confinement effect on Wannier-Mott type excitons.

1. INTRODUCTION

For the last years our research groups at the National Aviation Academy of Azerbaijan, Scientific-Research Institute of Transport and Aviocosmic Problems, and the TÜBITAK, Marmara Research Centre, Materials Institute have been focused on layered semiconductors, specifically, GaSe, InSe and GaS due to increasing interest of their NLO and other applications (photovoltaics, particle detection etc.). We used the LA (Laser Ablation) method to obtain the nanoparticles of these materials with a given size and to examine elemental content (XRF- X- ray Fluorescence, GDOES- Glow Discharge Optical Emission Spectroscopy), structural (X- ray, TEM- Transition Electron Microscopy, and SEM- Scanning Electron Microscopy), optical (absorption in VIS- Visible, near-, and mid- IR- Infrared, PL (photoluminescence) also in confocal geometry), vibrational (Raman and confocal Raman spectroscopy).

2. METHODOLOGY

The starting materials were prepared by mixing quantities of high-purity (99.999%) gallium and sulfur pellets in the atomic proportion 1/1. Especially un-doped GaS crystals were grown by the Bridgman-Stockbarger method in an evacuated quartz tube (10^{-5} Torr). GaS single crystals 20 mm in diameter and 60 mm in length with yellow color were successfully obtained.

Nanoparticles were grown by home built LA apparatus during stay of Prof. K. Allahverdiyev at the Institute of Material Sciences, Tsukuba University, Tsukuba, Japan (Prof. K. Allahverdiyev are indebted to Prof. S. Onari for his hospitability during stay at Tsukuba University). KrF Excimer laser at 248 nm (COHERENT COMPex 201), with the repetition frequency f = 10 Hz and pulse duration $\ddagger = 10$ ns, 25 mJ and 200 mJ pulses were used and the particles were deposited at different gas pressures. In the present paper the results only for nanoparticles deposited onto the quartz plates will be presented and discussed.

3. RESULTS

Growth from the melt (Bridgman method) provided large single crystals sufficiently homogeneous and free of defects which allows the fabrication of samples destined for optical or transport phenomena measurements. A little thin slice of single-crystal sample was ground into

powder and its XRD pattern was recorded. The results showed the presence of diffractions characteristic of hexagonal phase for GaS (D_{6h}^{4} space group). The XRD pattern indicated that the as-prepared products have high crystallinity. The cell parameters are in agreement with that presented in [1]. Elemental content analysis of grown crystals are as follows: the results obtained by the GDOES confirmed nearly stoihciometry content (49.5 at % of Ga and 49.3 at% of S). XRF measurements performed on series of GaS crystals showed nearly the same content. Energy dispersive X-ray spectrometer (EDS) analysis indicated only presence of O (oxygen) element in the spectrum, indicating the high purity of grown crystals.

The average size of grown GaS nanoparticles were controlled by a change in the pressure of the noble gases and the laser energy. The size of grown particles was estimated by direct observation with a TEM operated at 200 kV. All measurements were carried out at room temperature.

The particles with the size in the range of 5 - 10 nm were obtained at conditions- when the shape of plume was close to the theoretical one (upper right Picture presented in Fig. 1).

Spectral dependences of optical density of grown particles versus gas pressure (Ar and He) for GaS particles for different laser powers were built, analyzed and by using these data absorption gap versus gas pressure were built. It was established that characteristic feature of these dependences is that with increasing gas pressure optical density shifts to lower energies. It was seen that absorption gap increases with increasing pressure up to about 0.5 Torr (He gas, laser pulse power 200 mJ and He gas, laser pulse power 25 mJ) and then decreases. With increasing the distance between the target and substrate gas pressure value from which the gap of particles start to decrease and shifts to higher gas pressure (at ~ 0.1 - 0.14 Torr at distance 30 mm and at ~ 0.22 Torr at distance 60 mm).

We associate the blue shift in the optical absorption spectra of GaS with decreasing the particle sizes to the presence of nanocrystals in the quantum size regime (nearly same as it was reported earlier for GaS and InSe [2]). According to Brus [3] an analytical expression for the first excited electronic state of the quantum particle is:

$$E = \frac{h^2 f^2}{2R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\vee R} + \text{ polarization terms}$$
(1)

where: the first term is the quantum energy of localization; the second term is the Coulomb attraction; the third term (smaller term) arises from Coulomb interaction in the presence of a crystalline surface; R is the radius of the particle; m_e^* and m_h^* are the effective masses of electron and hole, respectively, and e is the charge of an electron, \vee is the dielectric constant at the optical frequency. The value of E represents the energy shift with respect to the value of the band gap for bulk crystal. It was shown, that for nanoparticles of GaS the combination of Coulomb term and relatively large effective masses (compared to GaAs, InSb etc.) keeps the excited state energy near the bulk forbidden gap for diameters larger than approximately 20 nm (very similar to that for GaSe and InSe).



Figure 1. Shape of plume formed during ablation in dependence on the gas pressure (less than 0.05 Torr- upper left; 0.5 Torr-middle; 1.5 Torr- right). Lower 3 pictures represent the TEM of GaS particles ablated at different He gas pressure (results are very similar to those obtained for GaSe crystals).

4. CONCLUSIONS

1. High optical quality crystals of GaS were grown by the Bridgman-Stockbarger method having a size of 20 mm in diameter and 60 mm in length.

2. The nanoparticles of GaS have been synthesized using LA method. The size of nanoparticles was successfully controlled by selection of the experimental parameters of rare gas species of Ar or He: at pressures lower than 0.1 Torr the particles with diameter more than 15 nm were obtained. Increasing the gas pressure more than 0.1 Torr results to formation of particles with diameter 5 nm and less (at gas pressure 1 Torr). Further increasing the pressure leads to increasing the particle sizes (12 nm at 5 Torr).

3. Blue shift in the optical absorption spectra of GaS with decreasing the particle sizes was explained by presence of nanocrystals in the quantum size regime. These results are consistent with a perturbation of GaS band structure due to carrier confinement, resulting in a widening of the forbidden gap.

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SENSING OF CONTAMINATIONS ON WATER AND EARTH SURFACES BY LIDAR DEVELOPED AT NAA

A.M. Pashayev, B.H. Tagiyev, K.R. Allahverdiyev, I.Z. Sadikhov*

National Aviation Academy (NAA)

ilham-sadixov@mail.com

A new laser induced fluorescence KA-14 LIDAR system for detecting of oil spills on the sea surface was employed at the National Aviation Academy of Azerbaijan. This LIDAR is the first performing these kind of research not only on the Azerbaijan beach of Caspian sea, but also on the earth places of Absheron peninsula, where oil-gas production takes place.

1. INTRODUCTION

The Light Induced Fluorescence method (LIF) has the unique capability to identify oil on backgrounds that include water, beaches, soil, ice, and snow. LIDAR (Light Identification Detection and Ranging) represents an active remote sensing technique used for atmospheric, water basins, soil and forestry monitoring [1]. If oils are irradiated by UV radiation, the light is absorbed and a portion of its energy is emitted as fluorescence. Different oils reveal different spectra [2].

For the last years our Lasers and Applications research group at the NAA of Azerbaijan, Scientific-Research Institute of Transport and Aviocosmic Problems have been focused on remote sensing of oil spills on a water surface. Fluorescence KA-14 LIDAR was developed and built.

2. METHODOLOGY

Developed LIDAR consists of three units: the laser emitter, receiver and spectrum analyzer. The third harmonics of a Nd:YAG ($\} = 1064$ nm) laser (QUANTEL, Big Sky Laser Series, CFR 200, $\} = 355$ nm, pulse duration 7 ns, repetition rate 20 Hz, energy per pulse 60 mJ, energy bistability < 2%, beam divergence < 3.5 mrad, beam diameter 5.35 mm) was used for the excitation of the fluorescence spectra of mineral oils spilled on a water and earth surface (latter have been taken from the places where oil-gas production takes place). The laser sends a pulse at wavelength of 355 nm toward the target object, causing the latter to fluoresce. The fluorescence signal is collected by a telescope (Newtonian- type) of 200 mm aperture and transmitted to the spectrum analyzer via the optical fiber.

Two types of spectrum analyzer have been used: • first- based on OMA ((Optical Multichannel Analyzer) (grating spectrometer (OCEANOPTICS, model Maya 2000 Pro) with CCD camera)). This analyzer allows registration of the detailed spectrum of fluorescence in the spectral range of 380 – 750 nm; • second- based on multichannel optical detector (LICEL GmbH, Multispectral LIDAR Detector. Spectral sensitivity is in the range of 300 – 880 nm). We used such an analyzer at a second stage, for the routine measurements (signal was detected in this case by the PMTs (Photomultiplyer)). This multispectral detector allows simultaneous detection of multiple spectrometer wavelengths. It is based on a multianode, metal- channel- dynode PMT. 32 photocatode elements together with 32 single photon counting systems provide 2-dimensional, spectral and range resolved data (range resolution- not less than 7.5 m).

The signal from the output of CCD camera (PMTs in the case of multichannel optical detector) is directed to the analog-to-digital converter, from where it continues to a computer, in

which signals are preprocessed and recorded. General view and technical parameters of developed LIDAR is presented in Fig. 1 and Table 1, respectively.



Figure 1. General view of the fluorescence KA-14 LIDAR developed at the NAA of Azerbaijan (upper and lower pictures). The laser sends a pulse at wavelength of 355 nm toward the target object, causing the latter to fluoresce. Part of the radiation is caught by the receiving telescope and transmitted to the spectrometer or to the multichannel optical detector.

Table 1.

Technical characteristics of KA-14 LIDAR for monitoring the liquid and solid dirty spices taking place on the water and earth surfaces during oil-gas production.

No	PARAMETER	VALUE
1	wavelength of laser excitation	355 nm
2	diameter of telescope (Newtonian- type)	200 mm
3	coefficient of multiplying the diameter of laser radiation by the collimator	not less than 3
4	range of angular measurements of telescope relative to horizon	from -20 to +20 degree
5	spectral resolution	6 nm
6	spectral range of measurements	300 – 800 nm
7	number of spectral channels	32
8	maximal distance of ranging	250

3. RESULTS

The typical fluorescence response of the Caspian Sea water covered by an optically thin oil film with UV laser source consists of wide band with a maximum in the UV range for light refined oils and in the visible range (420-490 nm) for the crude oils [2]. Our measurements were performed according to the next sequence: •first- background measurement was done with closed output of the laser beam (the laser was in operation); •then the measurements of the fluorescence spectra of given subject (oil, benzene and other spices) were performed; •finally, the background spectrum was substracted from the fluorescence spectrum of a given subject and required spectrum was registered for future analysis; •signal accumulation time was ~120 second. Some results of measurements performed by our LIDAR from the distances ~40 m are presented below. Fig. 2 represents the emission spectra of the Caspian sea water and crude oil on water surface. Spectra were taken from Kala Gas-oil Production Firm of the Absheron peninsula of Azerbaijan.

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Figure 2. Fluorescence spectra of sea water (left figure- brown curve) and oil spills on the surface of sea water (left figure- red curve) on a distnce of 60 m. Right Figure shows the difference between red and Brown curves. Peak at ~ 402 nm at right Figure is due to Raman scattering line of water and peak at ~ 532 nm are due to "technical peculiraities" of optical system, which do not allow to block totally second harmonic of 1064 laser line. It is seen that developed system allows to make reliable detection of oil spills on water surface by "Maya 2000" Ocean Optics system at least in the distance ranges of 40-60 m.

Measurements performed at Pirallahi Oil-gas Production Enterprize at Qala, Absheron peninsula, showed, that it is possible to measure oil spills at a distances up to 200 m The results will published later.

4. CONCLUSIONS

The research described above focuses on the following objectives: •fluorescence KA-14 LIDAR was developed at the NAA of Azerbaijan for detecting the oil spills and other dirty spices taking place on water surface of the Azerbaijan part of Caspian sea and dirty spices, taking place during oil-gas extraction; •preliminary results showed that developed LIDAR may be successfully used for the detection of the fluorescence pectra of oil spills on the Caspian sea water surface from the distances up to ~ 200 m.

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 $Ge_{1-x}Si_x$ [2],

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DEVOLOPMENT OF TECHNOLOGY OF OBTAINING AND STRUCTURE OF NANOCOMPOSITES BASED ON ISATACTIC PP AND MAGNETITE (Fe₃O₄)

A.M. Maharramov, M.A. Ramazanov, H.A. Shirinova

Baku State University, NanoResearch Laboratory

h.shirinova@bk.ru

Magnetic nanocomposites generally comprise of magnetic nanoparticles, embedded in polymer matrix. In the last few years, the need to obtain new lightweight and inexpensive magnetic materials promoted the devolopment of magnetic polymer based composites. In this work different amounts of magnetite (Fe_3O_4)nanoparticles were added to polypropylen matrix and nanocomposites were studied by optic microscope and SEM.

Nanoparticles of magnetite (Fe₃O₄)were synthesized by co-precipitation method from an aqueous solution, containing iron salts and a base, at room temperature in ambient atmosphere. As a result, the mean diameter of magnetite Fe₃O₄ nanoparticles varies from 7 to 15 nm. The morphology of synthesized powder was characterized by SEM microscope (JEOL-JSM7600F). The crystalline structure of magnetite nanoparticles was characterized by X-ray powder diffractometer (Philips X-pert). The magnetic polymer nanocomposites, containing these magnetite nanoparticles in isotactic PP matrix, were manufactured by ex-situ method. Composites were prepared with different amounts of magnetite nanoparticles, namely 1%, 3%, 5%, 7%, 10% by weight. Thickness and diameter of samples are equal to 100 µm and 4 cm.

The distribution of magnetite(Fe_3O_4) nanoparticles in the polymer matrix was studied by optical (Zeiss Axio Imager A2m) and scanning electron microscopy (SEM, Jeol JSM-767F)



Figure 1. Studies of the microstructure of the magnetic polymer nanocomposites by an optical microscope a) PP+5%Fe₃O₄ b) PP+7%Fe₃O

It can be seen from the Figure 1 that the distribution of particles improves with incresing of consentration.

Studies of the microstructure of the magnetic polymer nanocompositesnamely 5% and 7% by SEM are shown in Figure 2.



Figure 2. SEM images of nanocomposites

a) $PP+5\%Fe_3O_4$ b) $PP+7\%Fe_3O_4$

SEM images show that for PP+5%Fe₃O₄nanocomposite avarage size of nanoparticles is 16nm and for PP+7%Fe₃O₄nanocomposites avarage size of nanoparticles is 15nm.Agglomerations, occured in both case, which contain quite high content of Fe₃O₄ nanoparticles. But avarage size of nanoparticles in polymer is not so higher than initial size of nanoparticles.

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GaSe

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RAD AS YA L MOD F KAS YA OLUNMU POL PROP LEN (PP)

V GÜMÜ SULF D (Ag₂S) SASINDA PP/Ag₂S NANOKOMPOZ TL R N SONOEMULS YA ÜSULU L ALINMASI V QURULU U

M. . Ramazanov, S.Q. Nuriyeva, .A. M mm dli

Bakı Dövl t Universiteti

aliyeva-s@list.ru., i.ilahe199218@gmail.com

T dqim olunan i d kombinasiyalı metodla alınmı izotaktik polipropilen v gümü sulfid saslı nanokompozitl rin alınma texnologiyası i l nmi v polimer nanokompozitin qurulu unda ba ver n d yi iklikl r, nanohiss cikl rin forması, paylanması v ölçüsü t dqiq olunmu dur.

Son ill rd üzvi polimerl r daxil edilmi qeyri-üzvi nanohiss cikl r sasında alınmı materialların t dqiqind perspektivli n tic l r ld edilmi dir.Gümü sulfid (Ag₂S) nanhoss cikl rin mara ın artması onların unikal elektrik, termoelektrik, optik v fotoqolvonik xass l ri il ba lıdır [1-3]. T rkibind Ag₂S nanohiss cikl ri olan nanokompozitl r bu xass l rin gör gün elementi, yarımkeçirici, fotodetektor, sensor, ekranla dırıcı örtük, radio dal aların aktiv adsorberi v infraqırmızı üalanmanın polyarla dırıcısı kimi müxt lif cihazlarda geni t tbiq sah l rin malikdir [4-5]. Bundan ba qaAg₂S saslı polimer nanokompozitin xass l ri polimerin sintez üsuluna çox h ssasdır v polimerin qurulu undan kifay t q d r asılıdır. Polimer Ag₂Snanohiss cikl rinin matrisd ölçül rin v paylanmasına stabill dirici v qurulu yaradan molekul kimi t sir göst rir. Dig r t r fd n qeyri-üzviv üzvi materialların birl m si h r ikifazanın xass l rinin özünd c ml m sin v daha yax 1 n tic l rin ld olunmasına s b b olur [6].

Qeyd etm k lazımdır ki, b zi polimerl riradiasiya (γ - üa) il modifikasiya etdikd onların xass l rind d yi iklikl r yarana bilir. Bel üalanmanın t siri il ba ver n d yi iklikl raliml r üçün geni ara dırma mövzusu olmu dur. Polimerl rd qamma üaların t siri il d yi iklikl rin öyr nilm si mövzusu polimer üçün uy un stabil sistemin yaradılması baxımından da maraqlıdır. Mü yy n edilmi dir ki, radiasiya t siri polimerl rd kimy vi d yi iklikl rin, h mçinin tikilm l r, z ncirin da ılması, müxt lif kimy vi qrupların yaranmasına s b b olur.Onların optik xass l rini ara dırdıqda is qada an olunmu zonanın eninin azalması mü ahid olunur [7-9].

Polimer/yarımkeçirici nanokompozitl rinhazırlanması üçünbir çoxüsullari l nib hazırlanmı dır. T dqiq olunan i d is polipropilen (PP) v gümü sulfid saslı (PP/Ag₂S) nanokompozitinin alınması prosesind ultras s v mikroemulsiya metodlarını t tbiq edil r k kombinasiyalı alınma üsulu t qdim edilmi [10],h mçinin sintez zamanıpolipropilenin aktivliyiniartırmaq üçün onun tozunu ⁶⁰Co izotopunun γ - üaları il müxt lifdozalarda (15, 30, 50 kGy) üalandırılmı v radiasiyanın polimer nanokompozitin qurulu una, morfologiyasına t siri öyr nilmi dir.

 γ üaların PP polimerinin qurulu unda hansı effektiv d yi iklikl r s b b olmasını mü yy n etm k üçün modifikasiya olunmamı, γ üaları il modifokasiya olunmu polimer v h min polimer sasında alınmı PP/Ag₂S nanokompozitin Q spektrl ri kil 1-d göst rilmi dir.

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k.1. Modifikasiya olunmamı PP(a), γ - üası il modifikasiya olunmu (b) PP v h min polimer sasında alınmı PP/Ag₂S (c) nanokompozitin Q spektrl ri

1167, 997 v 972 sm⁻¹ zolaqları polimerin izotaktik oldu unu göst rir. 2950v 2870-2880sm⁻¹ pikl ri 3 gruplarının asimmetrik v simmetrik valent r qsl rin ,2920v 2838sm⁻¹ 2qruplarının asimmetrik valent r qsl rin uy un g lir. üalanmadam sonra b zi pikl ri is xarakteristik pikl rin (1167, 997 sm⁻¹) yoxa çıxması mü ahid olunur. Bu da polimer z ncirin da 11ması dem kdir. 2838, 1462 v 1378 sm⁻¹ pikl ri d mü yy n d r c d itir. Bel likl metil v metilen gruplarının C-H rabit l ri gırılır.Dem k olar ki, üalanma CH₃ gruplarının sayını azaldaraq onları CH₂ qruplarına çevirir v polipropilen z ncirind tikilm 1 r s b b olur. γ üalanmadan sonra polimerd h r hansı bir k skin pikin yaranması mü ahid olunmur. Yalnız 3370-3400 sm⁻¹intervalında geni bir zolaq mü ahid olunur ki, bu da O-H hidroksil qruplarına üalanmanın t sirind n polimer z ncird uv un g lir. Bu is hidroksil qruplarının formala dı ını göst rir. H mçinin 1600-1715 sm⁻¹ dal a uzunluqları oblastında zolaqlar yaranır ki, bu da C=O qruplarının yaranması dem kdir. Bu yeni qrupların yaranması üalanma prosesinin vakuumda aparılmadı ından ir li g l bil r, y ni oksigen havadan götürül bil r. PP+Ag₂S nanokompozitinin Q spektrini t dqiqi 2838, 2722, 1716, 840 sm⁻¹ pikl rinin v 3370-3400 sm dal a uzunlu undakı intensivlikl rinin azalması görünür.H mçinin ilkin halda mü ahid olunan 1629, 1598 sm pikl ri d mü ahid olunmur. Bu is h min grupların Ag₂S nanohoss cikl ri il örtülm sin d lal t edir. N tic d üalandırılmı polimerin nanohiss cik üçün optimal mühit oldu unu anla ılır.

üalanma dozasının matrisd nanohiss cikl rin formala masına t sirini t dqiq etm k üçün kil 2-d ilkin m hlulların sabit konsentrasiyasında (0,01M), müxt lif dozalarda modifikasiya olunmu polimerl rd n alınmı PP+Ag₂S nanokompozitl rininatom qüvv mikroskopik (AQM) t svirl ri göst rilmi dir.

AQM t svirl rin t hlilind n görünür ki, γ üalanmadan sonra polimerin s thi daha hamar olur, y ni nümun nin s thinin qurulu u polimerd yaranan aktiv m rk zl rin hesabına d yi ir. H mçinin, γ üalanmanın dozasının artması il kompozitin h cmind Ag₂S nanohiss cikl rinin miqdarının d yi m si, y ni mü yy n qiym t kimi çoxalması mü ahid olunur.

Bel bir n tic y g lm k olar ki, polimerin bu nanokompozitd funksiyası t k ba layıcı kimi deyil, h m d gümü sulfid hiss cikl rinin aqlomerasiyasının qar ısını almaqdır. Dem li nanohiss cikl rin diametrini t sir ed n faktorların parametrl rini uy un seç r k idar etm k olar. Bel likl, γ üaların dozasını d yi r k nanohiss cikl rin formala ması, paylanması v ölçüsünü idar etm k olar. T dqiqatlar n tic sind gümü sulfid nanaohiss cikl rinin polipropilen matrisd bircins v homogen paylandı ı mü ahid olundu.

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k. 2. Müxt lif dozalarda üalandırılmı tozlardan alınmı PP+Ag₂S nanokompozitinin SEM t svirl ri: a) 0 kGy b) 15 kGy c) 30 kGy d) 50 kGy

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TACLI BO ALMANIN T S R ALTINDA POLYARLA MA PROSES N N PVDF/ZrO₂POL MER NANOKOMPOZ YA MATER ALLARININ QURULU U V LÜM NESSENS YA XASS L R N T S R

F.V. Hacıyeva, M.A. Ramazanov, A.M. R himli

Bakı Dövl t Universiteti, NanoAra dırmalar Laboratoriyası

mamed_r50@mail.ru

Verilmi i d taclı bo almanın t siri altında polyarla ma prosesinin $PVDF/ZrO_2$ polimer nanokompoziya materiallarının qurulu u v lüminessensiya xass l rin t siri öyr nilmi dir. Mü yy n edilmi dir ki, polyarla ma prosesi zamanı nanokompozisiyasının komponentl ri arasında yaranan fazalararası s rh dd yaranan yükl r hesabına yüks k daxili lokal sah yaranır v bu sah nin t siri altında nanokompozitl rd lav lüminessent m rk zl r yaranır v n tic d lüminessensiyanın intensivliyi artır.

Polimer matrisd yerl n fotoaktiv nanohiss cikl rin çox böyük kimy vi aktivliyi malik oldu undan onlar matrisd çox yüks k fazalararası qar ılıqlı t sirl r göst rir. Nanokompozitd nanohiss cikl rin ölçül ri formala an üstmolekulyar qurulu ların ölçül rin yaxın v ya b rab r oldu unda i 1 nt siri altında polimerin makromolekulları yarımkeçirici doldurucuda yeni lav lüminessent m rk zl r h y canlandırır [1-2]. Nanokompozisiyaların polyarla ma prosesi zamanı kompozisiyaların komponentl ri arasındakı maksvell relaksasiya müdd tinin f rqi hesabına fazalarası s rh dd elektrik yükl ri yı ılır v bu yükl r nanokompoziyanın komponentl ri arasındakı fazalararası qar 11ıqlı t sirl ri d yi ir. Nanokompozisiyalar 2 v ya daha çox v birbiril kompleks elektrofiziki v fiziki-mexaniki xass l rin gör k skin d yi n komponentl rd n ibar t oldu undan onlarda laylararası polyarla ma prosesinin ba verm si mümkündür. Bu prosesl rin ba verm ehtimalı polyarla ma raitind n, polimer matrisd v polimer-doldurucu s rh ddind yük t l 1 rin konsentrasiyası v d rinliyind n çox güclü asılıdır. Bununla ba lı taclı bo almanın t siri altında aparılan polyarla ma prosesinin nanokompozitl rin qurulu v lüminessent xass l rin t sirinin öyr nilm si çox böyük maraq k sb edir.

Verilmi i d tach bo almanın t siri altında ba ver n polyarla ma prosesinin PVDF+ZrO₂ saslı nanokompozisiyaların qurulu u v lüminessensiya xass l rin t siri öyr nilmi dir. Tach bo alma il polyarla ma prosesi iyn -müst vi elektrodlar vasit si il h yata keçirilmi dir. yn l rin diametri 0,3 mm, iyn v nümun t b q l ri arasındakı m saf 1 sm b rab r olur. Bo alma g rginliyi U_t≈6-9 V, bo alma müdd ti 5-10 d qiq t kil etmi dir. Nümun l rin qalınlı 1 100 mkm t kil etmi dir. T crüb d n vv l nümun l rin s thi xüsusi t mizl nmi dir. Daha sonra nümun l r yer ba lanmı elektroda yerl dirilmi v 6 kV g rginlikd nümun s thind n 6×10^{-3} m m saf d yerl dirilmi metallik iyn l r vasit si il taclı bo almaya m ruz edilmi dir [3].

H mçinin PVDF+ZrO₂ saslı nanokompoziyaların taclı bo almanın t siri altında polyarla madan önc v sonra qurulu u atom-qüvv t mikroskopu vasit si il t dqiq edilmi dir. Skanetm hava raitind rezonans tezliyi 40-97 Hs- v ucunun yrilik radiusu 20 nm b rab r olan plazmakimy vi üsulla hazırlanmı zondlarla ntegra-Prima skanedici-zond mikroskopunda aparılmı dır. Mü yy n edilmi dir ki, taclı bo almanın t siri altında polyarla madan sonra nanokompozisiyaların s thinin qurulu elementl rinin xırdalanması ba verir [4].

 $PVDF+1\%ZrO_2$ saslı nanokompozisiyaların lüminessensiya spektrl ri taclı bo almadan önc v sonra Cary Eclipse spektroflüorimetrind 300-700 dal a uzunlu u intervalında t dqiq

edilmi dir. Lüminessensiya spektrl ri nümun ni $\lambda_{ex}=265$ nm dal a uzunlu unda h y canlandırılmaqla alınmı dır. kil 1-d PVDF+ZrO₂ saslı nanokompozisiya materiallarının taclı bo almaya m ruz edilm d n önc v sonra lüminessensiya spektrl ri göst rilmi dir. kild n göründüyü kimi lüminessensiya spektrind 389 nm, 446 nm, 458 nm, 495 nm, 530 nm, 565 nm pikl r mü ahid edilir.Mü yy n edilmi dir ki, taclı bo almanın t siri altında polyarla madan sonra lüminessensiyanın intensivliyi artmı dır v bu artma dem k olar ki ZrO2nin polimerin matrisind ki bütün miqdarlarında mü ahid edilmi dir.



k. 1. PVDF+1%ZrO₂ saslı nanokompozisiya materiallarının taclı bo almadan önc (1) v sonra (2) lüminessensiya spektrl ri.

kild n göründüyü kimi, PVDF+ZrO₂ nanokompozisiyanın lüminessensiyasının intensivliyi sas n 330 nm, 360 nm, 378nm v 531 nm dal a uzunlu undakı pikl rd mü ahid edilmi dir. F rz edilir ki, polyarla ma prosesi zamanı PVDF+ZrO₂ nanokompozisiyasının komponentl ri arasında s rh d yükl r hesabına çoxlu miqdarda elektrik yükl r yaranır. Bu yükl r hesabına yüks k daxili lokal sah yaranır v bu sah nin t siri altında nanokompozitl rd lav lüminessent m rk zl r yaranır v n tic d lüminessensiyanın intensivliyi artır [5-6].

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THE TECHNOLOGY OF PREPARATION OF NANOCOMPOSITES ON THE BASE OF ISOTACTIC POLYPROPYLENE/TITANIUM NANOPARTICLES AND INVESTIGATION OF THEIR STRUCTURE

A.B. Ahmadova, F.V. Hajiyeva, M.A. Ramazanov

Baku State University, NanoResearch Laboratory

mamed_r50@mail.ru

In this paper we report of obtaining novel nanocomposite structures based on isotactic polypropylene and nanoparticles of titanium. The distribution of titanium nanoparticles in the polymer matrix was studied by optical (Zeiss Axio Imager A2m) and scanning electron microscopy (SEM, Jeol JSM-767F). The IR spectra reveal that after the introduction of titanium nanoparticles in the polypropylene matrix there is a significant decrease in the intensity of the band at 2950 cm⁻¹ and 2839 cm⁻¹ which indicate on weakening CH stretching vibrations in the spectrum of polypropylene. SEM studies of polypropylene (PP) and nanocomposites based on PP+Ti showed that the introduction of nanoparticles in polypropylene leads to change of the supramolecular structure of the polymer and forming of a relatively ordered structure with the introduction of 1% of titanium nanoparticles in the polymer.

As advanced technologies are expanding, the need for novel functional materials significantly increases. Nowadays, materials with a special combination of properties (e.g., magnetic-transparent, conductive-transparent, catalytic-magnetic, etc.) are strictly required. Materials based on nano-sized metals will surely represent an adequate solution to many present and future technological demands, since they exhibit both novel properties and unique properties combinations. In recent years, the number of researches devoted to engineering of materials with special and practically important physical properties based on polymer composites containing metals nanoparticles significantly increased.Polymeric nanocomposite materials, composed of two or more phases, require the development of physical and chemical basis of preparation of new active elements by means of modification of its structure and properties. Polypropylene (PP) at the present time is one of the most prevalent synthetic thermoplastic polymer, that is widely applied in many fields. When PP is combined with metallic nanoparticles such as titanium nanoparticles, their ratio, the degree of dispersion, and other characteristics of the filler, it is possible to prepare materials with a desired set of properties.

PP/Ti based polymer nanocomposites were prepared as follows: isotactic polypropylene was solved in toluene at a temperature of 120°C. Nanoparticles of titanium, which were obtained by electroexplosive technology, added to the polymer solution (the volume content of titanium1%, 3%, 5%, 7%, 10%) at a temperature of 120°C withoutcooling the polymer solutionand stirred for an hour to obtain a homogeneous mixture. The mixture was transferred to a Petri dish and dried in a vacuum oven in 24 hour. The thin film nanocomposite were obtained by hot pressing at the melting temperature of polypropylene and a pressure of 10 MPa. Cooling the film after hot pressing was carried out in water and the cooling rate was 20 degree/min.

Figure 1 shows the IR spectra of nanocomposites based on polypropylene with titanium nanoparticles.

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Figure 1. FTIR spectra for the pristine PP (1), PP+1%Ti (2), PP+3%Ti (3), PP+5%Ti (4)

The IR spectra reveal that after the introduction of titanium nanoparticles in the polypropylene matrix there is a significant decrease in the intensity of the band at 2950 cm⁻¹ and 2839 cm⁻¹ which indicate on weakening CH stretching vibrations in the spectrum of polypropylene. The distribution of titanium nanoparticles in the polymer matrix was studied by optical (Zeiss Axio Imager A2m) and scanning electron microscopy (SEM, Jeol JSM-767F). The surface of nanocomposites based on PP+Ti was studied by optical microscopy at various volume content of titanium. It was found that with increasing concentration of Ti nanoparticles the larger agglomerates formed in a matrix. SEM studies of polypropylene (PP) and nanocomposites based on PP+Ti showed that the introduction of nanoparticles in polypropylene leads to change of the supramolecular structure of the polymer and forming of a relatively ordered structure with the introduction of 1% of titanium nanoparticles in the polymer.

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TOPOLOG CAL INSULATOR BASED PHONON C

CRYSTALS:FUNDAMENTAL AND APPL CAT ONS

A.M. Mamedov

Bilkent University, Ankara, Turkey

mamedov@bilkent.edu.tr

It is well known that metamaterials are artificially designed composite materials which can exhibit properties that cannot be found in nature. These properties can be electronic, magnetic, acoustic, or elastic and have, of late, come to include static properties [1]. In the context of acoustic metamaterials (AMM), these properties refer to the bulk modulus and density, and for elastic metamaterials, they refer to the moduli (bulk, shear, and anisotropic) and density of a designed composite material. AMM have the potential to achieve unique, unprecedented effective acoustic properties [2] while maintaining reasonable sample sizes. Analogous to their electromagnetic counterparts [3], these materials utilize engineered deep subwavelength microstructures, making effective-medium theory and effective properties appropriate. Unprecedented anomalous effective properties have been predicted and demonstrated using these designs, with negative acoustic and elastic properties drawing major interest due to the implications of new interface and shear modes, evanescent wave enhancement, and reversal Doppler effect and refraction [3].

On the other hand phononic or sonic crystals [2] utilize structures with periodic high impedance inclusions in a low impedance matrix. Numerous novel phenomena have been demonstrate using these crystals (focusing, negative refraction, tunneling, and wave guiding). Physically, these phenomena are caused by Bragg scattering in an array of unit cells near the first Brillouin-zone edge, when the wavelength in the matrix is comparable to the periodicity [4].

In the present work the acoustic band structure of a two-dimensional (2D) phononic crystal (PC) containing an organic ferroelectrics and topological insulator were investigated theoretically and numerically by the plane-wave-expansion (PWE) method [5]. Two-dimensional PC with square lattices composed of topological insulator cylindrical rods embedded in the organic ferroelectric matrix are studied to find the existence of stop bands for the waves of certain energy. This phononic bandgap - forbidden frequency range -allows sound to be controlled in many useful ways in structures that can act as sonic filters, waveguides or resonant cavities. Phononic band diagram $\tilde{S} = \tilde{S}(k)$ for a 2D PC, in which non dimensional frequencies a/2 c (c-velocity of wave) were plotted versus the wavevector k along the -X-M- path in the square Brillouin zone (BZ) show four stop bands in the frequency range 0.01-8.0 kHz. The ferroelectric properties of matrix and unusual properties of topological insulator give us ability to control the wave propagation through the PC in over a wide frequency range.

We study the 2D composites by solving the basic acoustic wave equation and use Bloch wave analysis to identify the band gaps.

The numerical results for the band structure are expressed in terms of the normalized or reduced frequency , which is an expression of (a/2 cl) and it ranges from 0 to 3.0. The calculated band structures of the 2D phononic crystal shown that there exists complete acoustic band gaps for the assumed model around 0.4 to 2.8. The complete band gap along the right-handed triangle -X-M- with vertices at =(0,0), X = (, 0) and M =(,) show us that the entire angular range of the wave propagation direction, while other directions are not forbidden within a certain range of frequencies. The density of states (DOS) as a function of frequency

were also computed. The phononic DOS were calculated by sampling k-points in the 2D BZ. We found the density of states as a function of frequency by doing a sum of all the bands over all the frequencies. DOS calculations are particularly important since some physical properties, such as thermal conductivity and specific heat, can be modified by changing the phonon density of states in a phononic crystal. Briefly, they provide insight into the microscopic and macroscopic properties.

The dispersion relation, (k), for the first and second bands were calculated. For this calculation, we have to calculate the full band diagram for all k-vectors in the first BZ, not like the band diagram calculated only along the -X, X-M, and M- directions in the first BZ. Like the band structure construction, we used the frequency-domain PWE method to create the equifrequency contours (EFC). They are illustrated in Figure. The plots provide a better understanding of how such dispersion influences acoustic velocity. Moreover, the contour plots of the associated dispersion surfaces are shown in figure. The EFC are at the intersection of the 3D dispersion curves with a horizontal plane and they provide an essential source of information. Eigenfrequency contours are especially informative about its qualitative shape.



Figure 1. (a) The dispersion, (k), relation (band-diagram) for the first bands of the square phononic crystal, calculated for all k-vectors in the first Brillouin zone. (b) The equifrequency contours for the first bands zone.

By considering the acoustical wave vector and the group velocity as local parameters, the shape of the equifrequency contours can be used accurately to account for anisotropy. Circular dispersion in reduced k space means that the medium is an isotropic medium and the wavevector of the acoustic wave and the group velocity are parallel for any propagation direction. Therefore, in the material the velocity of the acoustic wave does not depend on the direction that the wave travels. As can be seen, the radius of the EFCs clearly increases as the frequency increases.

The equifrequency surfaces, of the incident wave along the -X-M- direction shows that local curvature of the EFCs deviates from circular symmetry. An equi-frequency plot of the 2nd band, which is a little bit more complicated than the 1st band, which exhibits a square-like contour. The case of a non-circular EFC, however, indicates anisotropic behavior. On the other hand, a square like contour also reflects some symmetry in a particular direction. This could especially be advantageous and even be more effective if the self collimation property of the phononic crystal is considered. It must be noted that the group velocity vg is normal to the equifrequency contour but not collinear to the wave vector k. At each frequency, the energy flow direction is given by the normal to the equi-frequency contour, and is in the direction of the maximum rate of change of frequencies. The calculated contours also allow us to analyze whether the phononic crystal can have negative density or not, depending on the sign of the dispersion slope. From the equi-frequency contour plots above, we can see that the radius of the circle increases with frequency. Hence, we can conclude that the dispersion slope is positive.

The unusually large angles ($\sim 180^{\circ}$) between the phase and group velocities of acoustic waves lead to many unusual wave phenomena observed at crystal-air or crystal-isotropic medium interfaces. In order to understand the dynamics of wave propagation, the concept of group velocity may be useful from the viewpoint of energy transportation. From [2], it follow that the envelope of the wave packet propagates with the velocity Vg. The direct calculation of the derivative of the dispersion relation calculated numerically is not always convinient and can give error. As shown in [2], the group velocity of the wave packet is equal to the velocity of energy transfer. Thus, by using the results of [2, 3] the group velocity can be always calculated more accurately, irrespective of the number of points in the dispersion curve. Therefore, we have calculated the group velocity along the high-symmetry directions -X-M- of the BZ. It is evident that the components of the group velocity versus the high symmetry direction (-X-M) vary over a wide limits. The dependences Vg, which describe the wave packets of localized modes of any order exhibit (generally) a maximum at certain propagation constants. This means that the dispersion of group velocity can be positive, negative or zero [2]. It is worth mentioning that the group velocity of the waves is zero at the high symmetric point X meaning that there is no energy transfer at this point.

In this paper, we initially discussed the band structure of two dimensional phononic crystal composed of a topological material embedded in a polymer host. We use the plain wave expansion method to calculate band gaps in the acoustic band structure of the locally resonant phononic crystal. The results of this study illustrate that the width of the first band decreases and more phononic stop bands appear under the assumption of the fluid/solid approach. The findings of this paper may be useful to the improvements in the design of acoustic phononic crystals and they provide some perspectives in a way for designing acoustic filters or insulators.

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FACILE SYNTHESIS AND STRUCTURE OF GERMANIUM NANOPARTICLES AND THEIR INTERACTION WITH BODY CELLS Osman Ersoy, Alı Karatutlu*, Mingying Song**, Ann P Wheeler***, Yuanpeng Zhang**** and Andrei Sapelkin****

Queen Mary University of London, London, United Kingdom, o.ersoy@qmul.ac.uk *Queen Mary University of London, London, United Kingdom, yuanpeng.zhang@qmul.ac.uk **Queen Mary University of London, London, United Kingdom, a.karatutlu@qmul.ac.uk ***Queen Mary University of London, London, United Kingdom, n.tarakina@qmul.ac.uk ****Queen Mary University of London, United Kingdom, a.wheeler@qmul.ac.uk ****Queen Mary University of London, United Kingdom, a.sapelkin @qmul.ac.uk

A one-step bench top chemistry route to the synthesis of germanium (Ge) nanoparticles (NPs) around 3 nm in size were shown by using GeCl₄ as a precursor. It was indicated that this facile method can be utilised in ambient air and temperature so it has more advantages than the other synthesis routes. Luminescent free-standing Ge NPs were prepared as suspended in water or ethanol. In ethanol, photoluminescence emission of the Ge NPs was observed between 700-800 nm. Optical and morphological features of Ge NPs were correlated using transmission electron microscopy, X-ray diffraction, Raman spectroscopy and photoluminescence spectroscopy. The structure of the particles was determined by a core/shell model with a small crystalline core and an amorphous outer shell with a surface that was terminated by hydrogen. Investigation of toxicity of Ge NPs in HeLa cells was carried out and compared with commercial carboxyl coated Cd/ZnSe quantum dots. The toxicity test showed that Ge NPs are less toxic compared to commercial CdSe quantum dots.

M SAM L S L S UM TOZUNUN K MY V

A ILAMA METODU L ALINMASI

F. . Rüst mov, N.H. D rvi ov, M.Z. M mm dov,

V.E. Ba ıyev, Y.Y. Bobrova, H.O. Qafarova, Z.A. A amalıyev

Bakı Dövl t Universiteti, Fizika Probleml ri ET

M sam li silisium ununun kimy vi a ılama metodu il alınma texnologiyası i l nmi dir. P- v ntipli silisium ununun kimy vi a ılanması modifikasıya olunmu $HF:HNO_3$: CH_3COOH m hlulunda oksidl diricinin çatı mazlı ı rejimind aparılmı dır. Alınmı nümun l rin morfologiyası v fotolyuminessensiya xass l ri t dqiq edilmi dir.

M sam li silisium tozu ad t n iki texnoloji üsulla alınır. Birinci üsulda m sam li silisium t b q si elektrokimy vi v ya kimy vi a ılama üsulu il silisium lövh si üz rind alınır. Sonra bu t b q silisium lövh sind n ayrılaraq, ultras s vannasında üyüdülür. N tic d m sam li silisium t miz kild tozu alınır [1]. Lakin bu üsulla praktiki t tbiq üçün lazım olan q d r m sam li silisium tozu hazılamaq problemlidir v baha ba a g lir. kinci üsulda vv lc silisium kristalı mexaniki yolla kür vi d yirmanda üyüdülür, sonra alınan toz d n l ri uygun a ılayıcı m hlulda kimy vi a ılanmaya m ruz qalır. Ad t n a ılama üçün t tbiq edil n m hlul 4:1:20 h cmi nisb tind götürülmü HF (49%), HNO₃ (65%) v H₂O qarı 1 ından ibar tdir v m sam li silisiumun formala ma reaksiyasının arasık silm z etm k üçün m hlula t dric n HNO₃ damcıları lav olunur [2]. Bu halda alınan tozlar d n cikl ri silisium kristallitl rinın üz rini nazik s thl örtmü m sam li silisium almaq olur, lakin bu üsulun çıxı 1 kifay t q d r azdır. Bundan ba qa bu m hlulu k silm z v intensiv olaraq qarı dırmaq t l b olunur. Bu da onunla laq dardır ki, m sam li silisium qidrofobdur v suda islanmır.

Bu i d m sam li silisium tozunun modifikasiya olunmu m hlulda alınması metodikası i l nmi dir. vv l p- v n -tip silisium t b q l ri kür vi d iyirmanda üyüdül r k hiss cikl rinin ölçül ri 5 mkm- d n kiçik olan silisium tozu alınır. A ılayıcı m hlul olaraq 1200:1:800 h cmi nisb td götürülmü plavik tur usu (49%), nitrat tur usu (65%) v sirk tur usu qarı 1 1 seçilmi dir. A ılayıcı m hlulda sirk tur usunun kifay t q d r olması silisium ktistallitl rinin yax 1 islanmasını t min edir. A ılanma ffaf polipropilen qabda maqnit qarı dırıcısının üstünd aparılır. vv l qaba silisium tozu, sonra is a ılayıcı m hlul tökülür. Qabarcıqlarla mü ayi t olunan reaksiya bir d qiq d n sonra ba layır. M sam li silisium toz d n l rinin alınması m hlulun s thin onların çıxması il mü ayi t olunur ki, onlar da m hlulun s thind n yı ılırlar. Bu prosesd zaman keçdikc reaksiyanın sür ti azalır, ona gör m sam li silisiumun formala masının arasık silm z edilm si üçün m hlula periodik olaraq damcılarla nitrat tur usu lav edilm li v m hlul arada arabir qarı dırılmalıdır ki, onun bütün kristallitl r t sirini t min etm k mümkün olsun.

Göst ril n üsul il alınmı m sam li silisium tozu vizual olaraq qonur-narınci r ngd olub otaq temperaturunda qırmqızı r ngli fotoluminessensiyaya malıkdir.

kil 1-d silisium tozunun kimy vi a ılanmadan vv lki v sonrakı 900 v 45000 böyütm l rd SEM kill ri verilmi dir. Göründüyü kimi kristallitl rin s thind alınan m sam li silisium s thin morfologiyasını tam d yi ir v s th nahamar olur.

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kil 1. Kristallitl rin s thinin m sam li silisiumsuz (a v c) v m sam li silisium qatının yaranmasından sonra (b v d) SEM t sviri.

Alınmı m sam li silisium tozunun fotoluminessensiyasının üalanma spektrl ri t dqiq edilmi dir (kil 2). üalanma spektrl ri 320 nm dal a uzunlu undakı i ıqla h y canlanmı dır. Bütün nümun l r otaq temperaturunda, yarımeni 0.85 eV olub, fotoluminessensiyanın maksimumu 661 nm- dü n qırmızı luminessensiya malıkdirl r v bu silisium lövh l ri üz rind alınan m sam li silisiumun üalanma spektrl rin tam uy undur [3].



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ZnO

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ZnO

ZnO/PMMA.

ZnO,

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EFFECT OF ION IMPLANTATION ON OPTICAL PROPERTIES OF NEAR SURFACES LAYERS ON KR⁺ IMPLANTED GAAS: SE AND RBS INVESTIGATION

M. Kulik^{1,2}, E.B Asgerov^{1,3}, A.P Kobzev¹, M. Latek⁴

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, 141980,

²Institute of Physics, Maria Curie-Skłodowska University, Poland 20-031, Lublin Poland ³National Nuclear Research Centre, 370143, Baku, Azerbaijan

⁴Institute of Electron Technology, A.I Lotnikow 32/46, 02-668W Warsaw, Poland

The optical constants refraction and extinction indexes of the near surface layers of GaAs after and before Kr^+ ions implantation have been studied by spectroscopic ellipsometry SE in the wavelength range from 250 nm to 900 nm. The samples of semi-isolating crystals were double irradiated with 250 keV and 100 keV. The total fluences were $1x10^{13}$ cm⁻² and $1x10^{16}$ cm⁻². After this process the samples have been exposed to ambient air for one month. In that time the irradiated surfaces were covered by native oxide layers. Then the ellipsometric spectrum of angles () and () were measured at three incidence angles 65° , 70° and 75° .

The thickness of the implanted layers were determined form the Rutherford Backscattering spectrometry RBS. The energy and the ions doses were so chosen to receive parallel flat layers enriched in krypton atoms in the near surface layers. The thickness of the native oxides layers were obtained on the basis of measurements with resonance nuclear reaction ${}^{16}O($, $){}^{16}O$ NR.

The refraction and extinction coefficients spectrum have been obtained by VASE software code. In this calculations of optical properties was described the implanted layers with the paramagnetic model of the dielectric functions. In these study ware obtained the average values of pseudo dielectric functions.

It was assumed that the thickness of the near surface layers are homogenous and the optical parameters of the native oxides on the implanted samples are the same like before implantation. It was notice that the both methods optical and nuclear are good describe the implanted near surface layers.

MEMRISTIVE EFFECT IN TIGaSe₂ SINGLE CRYSTALS irHasan Yu. Seyidov^{1,2*}, Rauf A. Suleymanov^{1,2}, Yasin ale¹, Serdar G ren¹, and Emir Suad Olcay¹

¹Department of Physics, Gebze Institute of Technology, 41400, Gebze, Kocaeli, Turkey ² Institute of Physics of NAS of Azerbaijan

rauf_suleymanov@gyte.edu.tr

Non - volatile memory or non-volatile storage is a computer memory that can get back stored information even when not powered. Non -volatile memory means that when the computer is shut down, anything contained in memory are served. Such type of memory not only would save energy, but it would allow for computers to be turned on and off almost instantly, by passing the slow start -up and shutdown sequence. Non-volatile memory may eliminate the need for

comparatively slow forms of secondary storage systems, which include hard disks. Modern semiconductor nonvolatile memories, such as flash memory have been successfully scaled down to achieve large capacity memories through improvements in photolithography technology. However, conventional memory scaling is expected to come up against technical and physical limits in the near future. In order to overcome this problem, new materials or structures have been proposed as a new alternative to the conventional scaling technology. Recently, a new candidate has emerged: resistance random access memory (ReRAM). It is based on new materials which show a resistive switching phenomenon. The ReRAM memory cell has a capacitor -like structure composed of semiconducting material sandwiched between two metal electrodes. Because of its simple structure highly scalable memory structures have been proposed. In the resistive switching phenomenon, a large change in resistance occurs on applying voltages, and the resistance of the cell can be set to desired values by applying the appropriate voltage. Recent studies have shown that the switching speed can be faster than several nanoseconds. However, driving mechanism for such ReRAM has not been developed. Therefore, elucidation of a driving mechanism is currently a very important issue in the development of ReRAM. Detailed experimental and theoretical studies on the resistive switching phenomenon must be carried out to determine the driving mechanism, and some possible models must be proposed. Besides, new materials suitable for using in ReRAM structures becomes extremely important both from physical and technological points of view.

The last years a new approach or more strictly speaking, **a new philosophy** has been developed and widely used considering the resistive switching phenomena - it is the conception of so-called "**memristor**" which was introduced by Leon Chua in 1971 [1].

The term "memristor" contain two basic concepts - memory and resistance. A memristive system is a passive device that cannot store energy, but that remembers the total charge transfer due to the metastable changes of its conductance. The key attribute of a memristor is that the resistance of switching depends not on the instantaneous value of the applied voltage rather on the entire **dynamical history** of the charge flowing in the system. Thus the memristor devices provide a new hot issue in the field of electronics and materials sciences.

Memristors are currently under intensive study by various research groups due to its potential for next generation nonvolatile memory applications, crossbar latches as transistor replacements, analog computation and circuit applications, circuits which mimic neuromorphic and biological systems. Hewlett - Packard Laboratories succeeded in fabricating a memristor based on TiO_2 film in 2008, which consists of a TiO_x and a stoichiometric TiO_2 thin layer, sandwiched between two platinum electrodes [2]. Since 2008, other transition metal oxides have been studied to explore memristor effect, including ZnO, VO₂, and TaO.

The mechanism of memristor is still a controversy. It is usually proposed that migration of charged oxygen vacancies results in the continuous change between low resistance states and high resistance states. Other explanations have been proposed such as memristive filament model, electron trapping -detrapping effect, modification of the interface between electrode and materials, etc.

Several nanofabricated devices have been found to manifest memory effects similar to those predicted by Chua. In these structures, the memory effects depend on charge carrier rearrangement at the nanoscale due to external perturbations. All memristors exhibit a distinctive "fingerprint" characterized by a **pinched hysteresis loop** confined to the first and the third quadrants of the I-V plane.

Electrical resistance switching effect is a phenomenon that has been recently discovered in TlGaSe₂ layered semiconductor by researchers offering this presentation [3]. It was

experimentally observed that electrical resistance in TlGaSe₂ can be switched reversibly by an electric current flowing between a high resistance state and a low resistance state. Surprisingly, the memristive switching effect has been discovered by us in bulk semiconductor material including the "fingerprint" of memristive behavior - pinched hysteresis loops, Fig.1.

Thus, we consider the TlGaSe₂ layered crystal and probably other crystals from the same family (TlInS₂, TlGaS₂, etc) as new type semiconductor materials suitable for using in ReRAM devices. Moreover, due to the long time investigations of these materials in our group, we have chances to establish the mechanism of memristive behavior investigating these materials. We think also, that semiconductors with layered crystalline structure may be very perspective constructing memory switching devices, because Me-Semiconductor-Me structures usually used in such devices are faced often with the problem of the quality of the surfaces of semiconductors which have the extremely high quality of the crystals surfaces.

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$TlSbS_2 < 3\%Ga >$	TISbS	² · 300		, σ _{ac} ~f ⁽).8 [,] T	'lSbS ₂ (2).
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	{ac} ($f(f) = \frac{f^3}{96}e^2kt$	$[7]$ $TN{\rm F}^2 a^5 f \bigg[$	$\left[\ln\left(\frac{-ph}{f}\right)\right]^4$,		(1)
e- ; a=1/α -	; <i>k</i> –	; α $\psi \sim e^{-\alpha r}$; $v_{ph} -$; N _F	-			
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9.6×1	0^{18} 1.23×10 ¹⁹	F -1 -3			TlSbS ₂ (R)	TlSbS ₂ <3	%Ga>
		$R = \frac{1}{2} \ln t$	$\left(\frac{-\mathrm{ph}}{f}\right).$				(2
84	(94Å,	2)	R	R	TlSbS ₂ 6	TlSbS ₂ <3	%Ga>
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$TlSbS_2 < 3\%Ga >$.	[6]		: 1.7	' × 10 ⁻⁷	TlSbS ₂	6.3×10 ⁻⁷	(4
		$\Delta E = 3/(2$	$R^{\circ} \cdot N_{\rm F}$:)	84	46 ,	(4
		$N_t = N_F \cdot \Delta$	ΔE				(5)
	: $N_{\rm t}$ =8.1×10 ¹⁷	- ³ TlSbS	$S_2 5.7 \times$	10 ¹⁷ -3	TlSbS ₂ <	3%Ga>.	

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elsenesedov@gmail.com

$$Ca(Al_{x}Ga_{1-x})_{2}S_{4}:Eu^{2+}(7\%) \qquad \begin{array}{c} (\) \\ =0.1, \ =0.2 \\ 4f^{6}5d \ 4f^{7}(^{8}S_{7/2}) \\ 500-600 \end{array}$$

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[8-10].

[7]:

$$E_a = A \cdot kT_{\max},\tag{1}$$

$$(0.86.10^{-4}), -$$
 15

[9]:

,

- 30[8], k -

s-

$$S = \frac{SE_a}{kT_{\text{max}}^2} e^{\frac{Ea}{kT_{\text{max}}}} , \qquad (2)$$

$$S \Box_t = \left(\frac{\beta E_a}{k T_m^2 N_c \cdot v_t}\right),\tag{3}$$

, –
$$(0,17 /c), N_c -$$

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. 1.

1.

Eu

,

 $Ca(Al_xGa_{1-x})_2S_4.$

(3)

(1), (2)

	T(K)	$E_a=25KT_m$ ()	$S_t(^2)$	S(⁻¹)
Ca(Al _{0,1} Ga _{0,9}) ₂ S ₄ :Eu7 ⁹	1) 95	0,204	1) 14,5×10 ⁻¹⁸	1) 8×10^{8}
	2) 165	0,355	2) 10 ⁻¹⁷	2) 10,4×10 ⁸
	3) 179	0,385	3) 4×10 ⁻¹⁷	3) 4×10 ⁹
	4) 232	0,5	4) 12×10 ⁻¹⁸	4) 12×10 ⁸
Ca(Al _{0.2} Ga _{0.8}) ₂ S ₄ :Eu7	1) 157	0,34	1) 18×10 ⁻¹⁸	1) 18×10^8
	2) 194	0,42	2) 13,2×10 ⁻¹⁸	2) 13,2×10 ⁸
	3) 239	0,5	3) 4×10 ⁻¹⁸	3) 4×10 ⁸
	4) 297	0,64	4) 6×10 ⁻¹⁸	4) 7,8×10 ⁸
Ca(Al _{0.3} Ga _{0.7}) ₂ S ₄ :Eu7	1) 102	0,22	1) 2,5×10 ⁻¹⁹	1) $2,5 \times 10^8$
	2) 133	0,286	2) 5×10 ⁻¹⁷	2) 5×10 ⁹
	3) 259	0,57	3) 2×10 ⁻¹⁷	3) 2×10 ⁹
	4) 339	0,73	4) 7,2×10 ⁻¹⁸	4) 7,2×10 ⁸
Ca(Al _{0,1} Ga _{0,9}) ₂ S ₄	1) 187	0,4	1) 14×10 ⁻¹⁸	1) $13,8 \times 10^8$
	2) 264	0,57	2) 9×10 ⁻¹⁸	2) 9×10 ⁸

[10],		,
	, ,	$10^{-12} \div 10^{-22}$ ² .
) b)) $10^{-18} \div 10^{-17}$ ² ,	$(10^{-15} \div 10^{-12} \ ^2) \\ (10^{-17} \div 10^{-15} \ ^2) \\ (10^{-19} \div 10^{-22} \ ^2) \\ 1,$	
, Ca(Al _x Ga _{1-x}) ₂ S ₄	Eu ²⁺ .	, ,

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SONOK MY V ÜSULLA KOBALT SULF D SASINDA NANOH SS C KL R N ALINMASI L.R. Q hr manh, M.B. Muradov

Bakı Dövl t Universiteti

qahramanli.lala@mail.ru

T qdim olunan i d kobalt sulfid nanohiss cikl ri etilenqlükolda sonokimy vi üsulula sintez olunmu dur. Difraktometrd n alınan n tic l r gör kubik fazada Co_9S_8 nanokristalları formala mı dır. Açar sözl r: kobalt sulfid, sonokimy vi üsul, nanohiss cikl r.

Hal-hazırda nanoqurulu lu materialların onların h cmi analoqlarından f rqli qeyri-adi xass l ri mü ahid olunmu dur. Fiziki v kimy vi xass l r hiss cikl rin ölçül ri, qurulu u v forması t sir göst rir. Kiçik ölçülü z rr cikl rd kvant ölçülü effektl r mü ahid olunur. Keçid metal halkogenidl rinin nanoqurulu ları – CdS, ZnS, HgS, PbS v CuS onların h cmi qurulu ları il müqayis d qeyri-adi fiziki v kimy vi xass l r göst rir [1, 2]. CoS –d metal holkogenid fazasına daxil olan bir üzvdür (CoS, CoS₂, Co₃S₄ v Co₉S₈) v kimy vi birl m l r baxımından mür kk bdir [3, 4]. Onlar unikal katalitik, elektrik, optik, magnit xass l ri v elektromagnit spektrd görün n v infraqırmızı rejim yaxın güclü daxili udması il laq dar xüsusi maraq do urur. Bu da kobalt sulfidin xass l rinin onun hiss cikl rinin ölçüsünd n, formasından, paylanmasından v s thind n k skin kild asılı olması xüsusi diqq ti c lb edir. Buna gör d CoS kristal strukturu v optoelektronik xüsusiy tl ri laylı qeyri-üzvi matrisl rin mikromühitind n kild asılı ola bil r. Onu da qeyd etm k lazımdır ki, xass l r, morfologiyaya v müxt lif stoxiometrik t rkib müxt lif sintez üsulları t sir edir. Bu xass 1 ri öyr nm k baxımından kobalt sulfidin nanohiss cikl ri, nanom ftill ri, nazik t b q l r kimi müxt lif morfologiyaları sintez etm k üçün bir neç s y göst rilmi dir. Müxt lif forma v ölçülü metal halkogenidl ri h m kimy vi, h m d fiziki hazırlanma üsulları il (hidrotermal/solvotermal metod, mikrodal alı üalanma, kimy vi buxarlanma çökdürm üsulu) hazırlanmı dır. Sonokimy vi proses nanostrukturlu materialların hazırlanmasında c lbedici metoddur. Proses daha vacib hiss cikl rin – ölçül rin paylanmasına, kiçik ölçül r, yüks k s th sah sin v yax ı termik stabilliy g tirib çıxarır. Faza t mizliyi asanlıqla ld olunur. Ultrasonik radiasiya kimy vi h llediciy t sir edildikd molekullar radiasiya tezliyin v daxili istiliyin artması hesabına titr m y ba layacaq. Kimy vi reaksiyada ultras s radiasiyasının effekti onun çox yüks k temperatur v yüks k t zyiqin olması il ba lıdır. Sonokimy vi h r k td iki istiqam t mövcuddur: Qabarcıqların daxili parçalanması v qabarcıqlar v maye arasında interfeys [1-5].

in m qs di kobalt sulfid nanostrukturun sonokimy vi metodla etilenqlükolda sintez etm kdir. Bu proses sad , maraqlı, geni miqdarda m hsul ld etm k üçün lveri li üsuldur.

T CRÜB H SS

Kobalt sulfid nanohiss cikl rini hazırlamaq üçün kobalt asetat kristalhidrat $Co(CH_3COO)_2 4H_2Ov$ natrium sulfidd n Na₂S 9H₂O 1:1 mol nisb tind götürülür. vv lc 3,5 qr Co(CH₃COO)₂ 4H₂O t r zid ç kilir, 20 ml etilen qlükol lav edilir v otaq temperaturunda qarı dırılır. Sonra 4,8 qr Na₂S 9H₂O t r zid ç kilib, 20 ml etilen qlükolda h ll edilib qarı ıq m hluluna lav olunur. Qarı ıq m hlul 35kHz tezlikd 1 saat ultras s qarı dırıcıda qarı dırılır. Alınmı qara r ngli çöküntü distill suyu il yuyulur v daha sonra etanolda bir neç d f yuyulub 80°C 24 saat havada qurudulur. Alınmı nümun rentgen difraktometrind t dqiq olunur.

N T C L R N MÜZAK R S

kil 1-d sonokimy vi üsulla 1 saat müdd tind alınmı m hsulun rentgen difraksiya analizi göst rilmi dir. Analizin n tic 1 rin gör PDF kartlarla müqayis d kubik fazada Co_9S_8 nanokristalları formala dı 1 (a=9,944Å) mü yy n olunmu dur.

k.1. Co₉S₈ nanohiss cikl rinin rentgen difraksiya analizi

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bbarhal@mail.ru

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p-Si-n-CuIn₅S₈ HETEROKEÇID N N ELEKTR K V FOTOELEKTR K XASS L R

L.H. H s nova¹, .Z. M h mm dov¹, A.A. hm d^2

¹Bakı Dövl t Universiteti, ²Az rbaycan Texniki Universiteti

rovshan63@ rambler.ru

Vakuumda termik buxarlandırma üsulu il p-Si lövh si üz rin $CuIn_5S_8$ nazik t b q si çökdürülm kl hazırlanmı heterokeçidin elektrik v fotoelektrik xass l ri t dqiq olunmu dur. H r iki yarımkeçiricinin parametrl ri n z r alınmaqla heterokeçidin energetik zona diaqrammı qurulmu dur.

 $CuIn_5S_8$ kristallı pinel qurulu una malik olmaqla kristal q f sind anion v ya kation vakansiyalarına malikdir. Bu defektl rin yaranmasına s b b olacaq atomların tetraedrik yerl m sind h r üç tetraedrd n birinin m rk zin atomun yerl m sinin mümkün olmadı ı göst rilir [1].

Kristal qurulu da yaranan bel periodik vakansiyalar onu defektli kristallar qrupuna aid edir. Vakansiyalar kristalın enerji diaqramında rekombinasiya m rk zl ri yaradırlar v bunlar da $CuIn_5S_8$ kristalının fotoelektrik v lüminessent xass l rind [2-4] mü yy n rol oynayırlar. p-Sin- $CuIn_5S_8$ qurulu u heterokeçid hazırlayıb, onun elektrik v fotoelektrik xass l rini t dqiq etm kl h r iki kristalın xass l rind ki xüsusiyy tl ri özünd c ml dir n yarımkeçirici cihazlar hazırlamaq olar.

d mikrosxem hazırlamaq üçün istifad olunan p-Si monokristal lövh üz rin vakuumda termik buxarlanma üsulu il $CuIn_5S_8$ birl m si çökdürm kl formala dırılmı p-Si-n- $CuIn_5S_8$ heteroqurulu un elektrik v fotoelektrik xass l ri öyr nilmi dir. $CuIn_5S_8$ birl m sinin nazik t b q sini almaq üçün xüsusi rejimli vuxarlandırma üsulu t tbiq edilmi dir. T rkibindi asan uçan kükürd komponenti olan $CuIn_5S_8$ birl m si ölçüsü bir neç mikron olan z rr cikli toz halında üyüdül r k vakuum buxarlandırma kamerasında temperaturu 1150⁰C- q d r köz rdilmi qrafit putanın iç risin mü yy n miqdarda tökülür. Bel rejimd buxarlandırılan birl m nin nazik t b q si h m p-S, h m d onun yanında yerl dirilmi NaCl lövh sinin üz rind alınmı dır. NaCl üz rind alınmı t b q nin t rkib v struktur analizi aparılmı dır. Bu t b q nin t rkibini v qurulu parametrl rinin buxarlandırılan madd nin t rkibi v parametrl ri il uy un g ldiyi

t stiql nmi dir.

p-Si-n- $CuIn_5S_8$ heteroqurulu unun 300 K-d volt-amper xarakteristikası kil 1-d t svir olunmu dur. Göründüyü kimi, qaranlıq raitd VAX-sı sırf diod xarakteri il ifad olunur (yri 1). Heterokeçidin düzün c r yan istiqam ti Si t b q y müsb t potensialın t tbiqi il mü yy n olunur. H cmi yükl r oblastında c r yankeçirm mexanizmi rekombinasiya-tunel prosesin uy undur.

ks g rginlikd c r yanın Ziner xarakterli oldu u göst rilir. Heterokeçid köz rm lampası il i ıqlandırıldıqda VAX 2 yri il t svir olunur. Heterokeçidi $CuIn_5S_8$ t r find n ıqlandıdıqda h ssaslıq oblastı 800 –1250 nm dal a uzunlu unu hat edir. Spektr h m Si, h m d $CuIn_5S_8$ kristalının fotoh ssaslıq oblastlarını hat edir. Spektrd mü ahid olunan ekstremal maksimumlarından biri (950 nm) $CuIn_5S_8$, dig ri (1100 nm) Si qada an olunmu zonalarının enin uy undur. Elektrik v fotoelektrik xass l rin t dqiqinin n tic l ri sasında heterokeçidin energetik zona diaqrammı qurulmu dur (k. 1, *a*).

k. 1. p-Si- CuIn₅S₈ heterokeçidinin VAX-1 v energetik zona diaqrammı (a): 1 qaranlıqda; 2 – i 1qda

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5CB NEMAT K MAYE KR STALININ ASTANA

G RG NL Y N BaTiO₃ NANOH SS C KL R N N T S R

M. . Ramazanov, A.R. mam liyev, . . Hümb tov

Bakı Dövl t Universiteti

shirxan-humbatov@mail.ru

Müasir ekranların maye kristal displeyd n ibar t olması onların ölçü v ç kil rinin kiçildilm sin rait yaradır. Texnikanın davamlı inki afı maye kristaldan ibar t qur uların texniki xarakteristikalarının yax ıla dırılmasını t l b edir. Bu üsullardan biri daha yax 1 maddi parametrl r malik olan maye kristalların sintez olunmasıdır ki, bu imkan getdikc m hdudla ır. Dig r üsul is maye kristallarla ba qa funksional materialların xass l rini konstruktiv kild laq l ndirm kdir. d istifad olunan BaTiO₃ nanohiss cikl rinin 4-pentil 4-sianobifenil (5CB) nematik maye kristalının sas elektrooptik parametrl rind n biri olan astana g rginliyin t siri öyr nilmi dir.

Ekperimentd nematik maye kristal olaraq geni yayılmı 4-pentil 4-sianobifenild n (5CB) v orta ölçüsü 600 nm olan BaTiO₃ nanohiss cikl rind n istifad olunmu dur.

5CB madd sind nematik maye kristal fazası 22 °C - 36 °C temperatur aralı ındadır v müsb t dielektrik anizotropiyasına malikdir: $v_u = 19.5$, $v_\perp = 6.7$, $\Delta v = v_u - v_\perp = +12.8$.

Barium titanat yüks k spontan polyarla maya malik olan seqnetoelektik material olub Küri temperaturu 120° C-dir². BaTiO₃ nanohiss cikl rinin maye kristalda dispersiya olunması xüsusi texnologiya sasında yerin yetrilir³. BaTiO₃ nanohoss cikl ri, olein tur usu v heptan 1:2:10 ç ki nisb tind qarı dırılır.

Maye kristalın dielektrik v elektrooptik xass l rinin t dqiqi elektrooptik yuvacı ın köm yi il aparılır. Elektrooptik yuvacıq t b q li (sendviç) qurulu a malik olub, bir-birind n dielektrik arak sm il ayrılmı, daxili s thi ffaf v keçirici (nazik In_2O_3) t b q il örtülmü iki parallel müst vi ü lövh d n ibar tdir. Planar orientasiya almaq m qs dil keçirici t b q nin üz rin nazik oriyentant t b q si ç kilir.

Elektrooptik yuvacı a doldurulacaq maye kristal t b q sinin qalınlı 1 teflon arak sm il nizamlanır v bo yuvacı ın elektrik tutumunu ölçm kl

$$d = \frac{\mathsf{V}_0 S}{C_0}$$

düsturu il d qiq t yin edilir. Burada $v_0 = 8,85 \ pF \ / m$ -elektrik sabiti, S- elektrooptik yuvacı ın i çi sah sidir, C_o -bo yuvacı ın elektrik tutumudur. Maye kristal displeyl rd v i ıq modulyatorlarında t tbiq baxımından elektrooptik yuvacı ın sas parametrl rind n biri U_{th} astana g rginliyidir. Bu parametri elektrik tutumunun g rginlikd n asılılıq qrafikind n t yin etm k olar. Elektrooptik effekt maye kristal mühitin effektiv dielektrik nüfuzlu unun, bunun n tic sind yuvacı ın elektrik tutumunun ($C = \frac{v_0 v S}{d} = v C_0$) d yi m sin s b olur. 5CB maye

kristalı müsb t dielektrik anizotropiyasına malik oldu undan elektrooptik effekt planarhomeotrop keçid klind dir. Bu keçidd maye kristalın dielektrik nüfuzlu u artdı ından t dqiq olunan yuvacıqda astana g rginliyi olaraq elektrik tutumunun artma a ba ladı 1 g rginlik götürülür.

BDU-nun Fizika Problerl ri nstitutunun yaradılmasının 10 illiyin h sr olunmu Beyn lxalq konfrans

kil 1. 5CB doldurulmu elektrooptik yuvacı ın volt-farad xarakteristikası

kil 2. 5CB+BaTiO₃ doldurulmu elektrooptik yuvacı ın volt-farad xarakteristikası

Eksperimental n tic l r

kil 1 v 2-d göründüyü kimi, t miz maye kristal olan yuvacıqda $U_{th} = 1,2V$ g rginlikd n ba layaraq elektrik tutumunun artması mü ahid olunur. Bu, yuxarıda qeyd olundu u kimi, maye kristalın planar orientasiyadan homeotrop orientasiyaya keçm si n tic sind effektiv dielektrik nüfuzlu unun artması il ba lıdır. Maye kristala BaTiO₃ nanohiss cikl rinin lav olunması voltfarad xarakteristikasında h miyy tli d yi iklik yaradır: tutumun $U_{th1} = 0,4V$ g rginliyind n ba layaraq z if, $U_{th2} = 2V$ g rginliyind n ba layaraq k skin artması mü ahid olunur. Bundan lav, BaTiO₃ nanohiss cikl ri lav olundu u maye kristal yuvacı ın volt-farad xarakteristikasında 6 V-dan ba layaraq tutumun bir q d r azalması görünür.

Volt-farad xarakteristikalarından o da görünür ki, planar -homeotrop keçid zamanı elektrik

BDU-nun Fizika Problerl ri nstitutunun yaradılmasının 10 illiyin h sr olunmu Beyn lxalq konfrans

tutumunun qiym ti t miz 5CB halında $\frac{C_{max}}{C_{min}} = \frac{2850}{1150} \approx 2.5$, 5CB+BaTiO₃ halında

is $\frac{C_{max}}{C_{min}} = \frac{325}{165} \approx 2$ d f artır. Bu is gözl nil n $\frac{V_u}{V_{\perp}} = \frac{19,5}{6,7} \approx 2,9$ qiym tind n xeyli a a ıdır.

Planar-homeotrop keçid h cmd ba layır v g rginlik artdıqca s thl r do ru yayılır. Güclü ili m halında s th yaxınlı ındakı molekullar az dönürl r, n tic d astana g rginliyind n d f l rl böyük g rginlikl rd bel alınan homeotrop orientasiya mük mm l olmur v dielektrik nüfuzlu unun $v_{II} = 19,5$ qiym ti alınmır.

BaTiO₃ nanohiss cikl ri lav edilmi kompozitd iki astana g rginliyinin alınması a a ıdakı kimi izah oluna bil r. N tic göst rir ki, 1% -li BaTiO₃ nanohiss cikl ri arasındakı orta m saf 10 mkm t rtibind dir v elektrik sah si olmadqda bu hiss sikl r spontan polyarla ması sıfır olur, y ni maye kristalın direktor sah sini t hrif etmir. Elektrik sah si t tbiq etdikd hiss cikl r polyarla araq öz lokal sah sini yaradır. Yuvacı a veril n g rginlik birinci astana g rginliyind n böyük olduqda bu lokal sah hiss cikl rin bilavasit s thi yaxınlı ındakı maye kristal molekullarının orientasiyasını d yi ir. Bu, maye kristalın dilektrik nufuzlu unu hiss olunacaq d r c d artırır. G rginlik artdıqca polyarla mı hiss cikl maye kristal molekullarının orientasiyası daha böyük m saf l rd d yi ilir. G rginlik ikinci astana g rginliyind n böyük olduqda nanohiss cikl rin t sir m saf si onlar arasındakı m saf t rtibind olur v bütün h cmd molekulların s th perpendikulyar düzülü ü ba verir. Bu is mühitin dielektrik nüfuzlu unun ikinci d f v k skin artmasına s b b olur. BaTiO₃ nanohiss cikl rinin lav olunmu maye kristal yuvacıqda planar-homeotrop keçidin iki m rh l d ba verm si elektrooptik ölçm l rl d t sdiq olunur [3].

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BDU-nun Fizika Problerl ri nstitutunun yaradılmasının 10 illiyin h sr olunmu Beyn lxalq konfrans

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4). k ₂	$\widetilde{n} = n_2 - ik_2.$ 1.		$n_1 = n_4 = 1$ (1 n_3, n_2
(3)		- 0 1 , 1 4	3. 3,
		$\{ = \left(\frac{4f}{3}\right)n_3d_3,$):
<i>d</i> ₃ –	T. R	: $T_0 = \frac{T_{34}}{\left(1 + R_{34}^2 - 2R_{34}\cos\{\right)},$, (2)
[10],	r_{34} r_{34} (3 4). $T_{34} = \frac{4n_3}{(n_3 + 1)^2}, R_{34} = \left(\frac{n_3 - 1}{n_3 + 1}\right).$	(3)
	}, . 0	, $ (d_3 > 2) $, $ \Delta \} = \} $ { $ \{ \qquad \{_2 \qquad \{_1, \dots \} \} $	>> }). $_{2}^{2}{1}^{2},$ $_{1}^{2} = \ell f + \Delta \{ ,$

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, d_3 , $\ell >> 1$,	>> } :
$T_0 = \frac{T_{34}^2}{1 - R_{34}} =$	$= \frac{T_{31}}{1+T_{34}} = \frac{2n_3}{n_3^2+1}.$ (5)
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