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Lasers in Synthesis, Characterization and Processing of Diamond

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12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release, distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The topic of the conference belongs to scientific and technology sphere where the progress goes very fast. Outstanding physical and chemical properties of diamond make it the material of choice for numerous advanced applications in optics (UV and high energy particle detectors, IR and millimeter waves windows, X-ray lithographic masks), mechanics (cutting tools for precision machining), acoustics (sound diaphragms, surface acoustic waves devices), electronics (heat spreaders, high-temperature sensors) and other industries. The conferences focuses on laser-based technologies, the topic which is often included in programs of different meetings on diamond materials, however it was never presented as the main topic at any meeting before. Participants will get more information about various diamond finishing procedures achievable with lasers, including surface smoothing, cutting, drilling, metallization, patterning. Researchers who are working on development of diamond synthesis techniques will discuss new laser-based methods of diamond deposition, which promise remarkably high growth rates. For those who are interested in reliable assessment of diamond quality the program will offer a variety of analytical methods (Raman spectroscopy, photoluminescence, laser flash, pulse photoconductivity, nonlinear absorption, etc.).				
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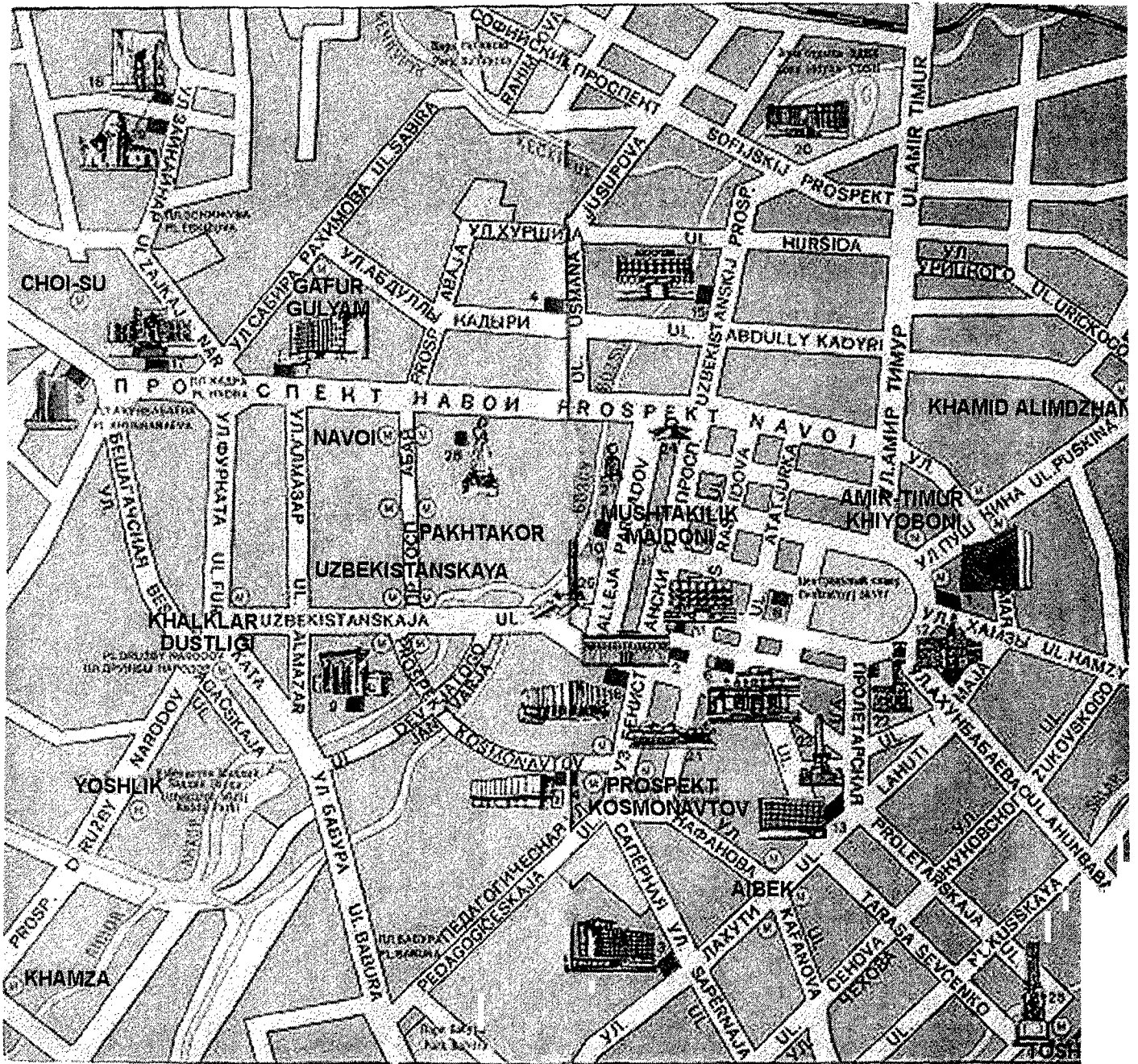
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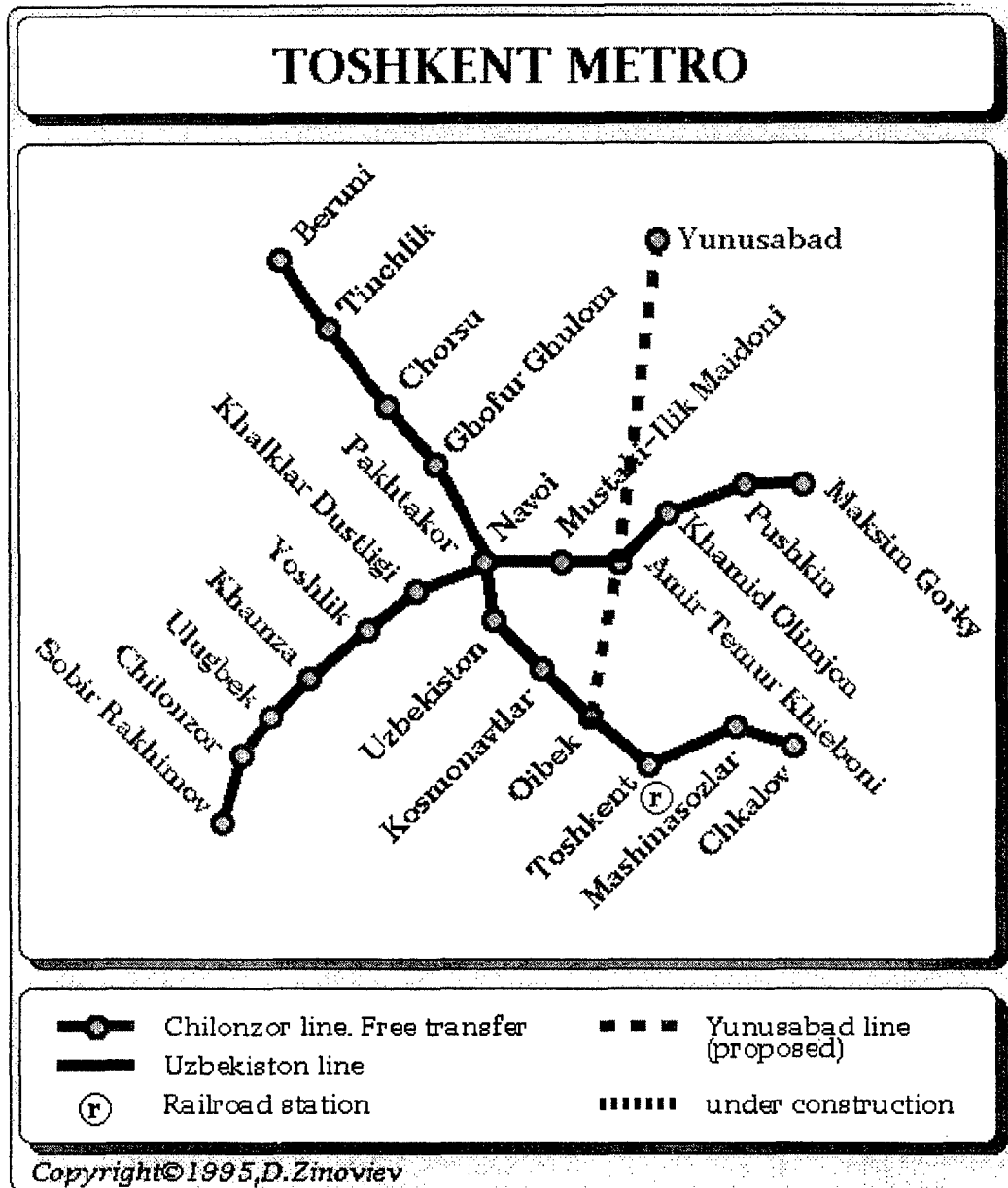
Map of Uzbekistan



Map of Tashkent



Sceme of Tashkent subway (TOSHKENT METRO)



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Program

Monday, 6 October 1997

	09:00	Registration	
	13:00	Lunch	
Session 1	14:30		Welcome and Introduction
Plenary session	16:00	1.1	(Invited) Precision Shaping of a Diamond Surface by Using an Interferometrically Controlled Laser-Ablation Method Sandor Holly ¹ , Victor Ralchenko ² , Sergej Pimenov ² , Taras Kononenko ² , ¹ <i>Boeing BNA; USA</i> , ² <i>General Physics Institute, Russian Academy of Sciences, Moscow, Russia</i>
	16:30	1.2	CO₂ laser driven plasma CVD of diamond and boron nitride films. V.I. Konov ¹ , S.A. Uglov ¹ , V.P. Ageev ¹ , A.M. Prokhorov ¹ , M.V. Ugarov ¹ , I. A. Leontiev ² , Dausinger ³ , B. Angstenberger ³ , G.Sepold ⁴ , S. Metev ⁴ , ¹ <i>General Physics Institute, Moscow, Russia</i> , ² <i>DiaGasCrown Ltd., Moscow, Russia</i> , ³ <i>IFSW, Stuttgart, Germany</i> , ⁴ <i>BIAS, Bremen, Germany</i>
	17:00	1.3	(Invited) In Situ Optical Investigation of Diamond Thin Film Growth A.M. Bonnot, <i>Laboratoire d'Etudes des Proprietes Electroniques des Solides, Centre National de la Recherche Scientifique, Grenoble, France</i>
	17:30	1.4	Chemical Vapor Deposition of Diamond Films on Nonuniformly Heated Substrates M.Kh.Ashurov ¹ , M.S.Saidov ² , T.M.Saliev ² , ¹ <i>«Phonon» Scientific Industrial Association, Tashkent, Uzbekistan</i> , ² <i>Physical-technical Institute of Uzbek Academy of Sciences, Tashkent, Uzbekistan</i>
19:00		Welcome reception	

Tuesday, 7 October 1997

Session 2 Deposition	09:00	2.1	Laser Ablation Deposition of Crystalline Carbon Nitride Films <u>A. Luches</u> ¹ , <u>A. Perrone</u> ¹ , <u>I.N. Mihailescu</u> ² and <u>M. Popescu</u> ² , ¹ <i>INFM and University of Lecce, Department of Physics, Lecce, Italy,</i> ² <i>National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, Romania</i>
	09:20	2.2	Laser Stimulation of Diamond Growth from Compressed Graphite <u>A.G. Molchanov</u> , <u>P.N. Lebedev Physical Institute, Moscow, Russia</u>
	09:40	2.3	QQC's Laser-Based Technology for Depositing Adherent Coatings on Engineering Tools <u>P. Mistry</u> , <i>QQC Company, USA</i>
	10:00	2.4	Deposition and laser damage tests of DLC coatings on quartz optical fibers and plates. <u>S.A. Garnov</u> ¹ , <u>V.G. Ralchenko</u> ¹ , <u>S.A. Uglov</u> ¹ , <u>E.D. Obraztsova</u> ¹ , <u>V.E. Strel'nitsky</u> ² , <u>A.V. Semenov</u> ³ , <u>V.M. Puzikov</u> ³ , and <u>B.E. Warner</u> ⁴ , ¹ <i>General Physics Institute, Russian Academy of Sciences, Moscow, Russia,</i> ² <i>Institute of Physics & Technology, Kharkov, Ukraine,</i> ³ <i>Institute of Single crystals, Kharkov, Ukraine,</i> ⁴ <i>Lawrence Livermore National Laboratory, CA 94550, USA</i>
	10:20	2.5	The Synthesis of Carbyne from Amorphous Linear-Chain Carbon and Pyrographite <u>M.B. Guseva</u> ¹ , <u>V.M. Babina</u> ¹ , <u>V.G. Babaev</u> ¹ , <u>M. Boustie</u> ² , <u>V.E. Fortov</u> ³ , <u>J.P. Romain</u> ² , <u>A.Z. Zhuk</u> ³ , ¹ <i>Department of Physical Electronics, Moscow State University, Moscow, RUSSIA,</i> ² <i>Laboratoire de Combustion et de Detonique UPR au CNRS ENSMA, Universite de Poitiers, FRANCE,</i> ³ <i>High Energy Density Research Center RAS, IVTAN, Moscow, RUSSIA</i>
10:40	Break		
Session 3: <i>In situ</i> control	11:10	3.1	(Invited) Resonance Enhanced Multiphoton Ionisation Probing of Hydrogen Atoms in a Diamond Hot Filament CVD Reactor <u>Michael N.R. Ashfold</u> , <u>Stephen A. Redman</u> , <u>Stephen R. Langford</u> and <u>Keith N. Rosser</u> , <i>School of Chemistry, University of Bristol, Bristol U.K.</i>
	11:40	3.2	Three-dimensional reconstruction of methyl density in a HFCVD reactor from CRDS experiments. <u>Y.A. Mankelevich</u> , <u>N.V. Suetin</u> , <i>Moscow State University, Nuclear Physics Institute, Moscow, Russia</i>
	12:00	3.3	Raman Spectroscopy for in-situ Study of Diamond Growth in DC Discharge Plasma CVD Reactor <u>A.N. Obraztsov</u> , <u>I.Yu. Pavlovsky</u> , <i>Physics Department of Moscow State University, Moscow, Russia</i>
13:00	Lunch		

Session 4: Spectroscopy	14:30	4.1	(Invited) Use of Laser Spectroscopies for the Study of a Diamond deposition Microwave Plasma Assisted CVD Reactor <u>A. Gicquel</u> ¹ , F. Silva ¹ , M. Dubus ¹ , A. Chiron ¹ , M. Chenevier ² , A. Lussaud ³ , E. Rzepka ³ , ¹ LIMHP CNRS- UPR 1311- Université Paris 13, , FRANCE, ² LPSB, Meudon, France, Université J. Fourier de Grenoble, France
	15:00	4.2	Diamond: a Material for Laser Spectroscopy <u>M.C. Castex</u> ¹ , D. Riedel ¹ , L. Museur ¹ , C. Chardonnet ¹ , A. Gicquel ² , F. Foulon ³ , C. Borel ³ , P. Bergonzo ³ , C. Jany ³ , ¹ Laboratoire de Physique des Lasers, Université Paris-Nord, Villetaneuse, France, ² Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions CNRS, Université Paris-Nord, Villetaneuse, France, ³ LETI (CEA-Technologies Avancées)/DEIN/SPE, CEA/ Saclay, Gif-sur-Yvette, France
	15:20	4.3	Laser Spectroscopic Study of Defects on HPHT Diamonds <u>I. Sildos</u> ¹ A. Osvet ¹ and A. Yelissev ² ¹ Institute of Physics, Tartu, Estonia, ² Institute of Mineralogy and Petrography, Novosibirsk, Russia
	15:40	4.4	Laser-Induced Luminescence Study of CVD Diamond Films with Different Microstructures. <u>S. Salvatori</u> ¹ , M. C. Rossi ¹ , F. Galluzzi ¹ , F. Somma ² , R. M. Montecelli ³ ¹ Dept. of Electronic Engineering, University degli Studi Rome TRE, Rome, Italy; ² Dept. of Physics, University degli Studi Rome TRE, Rome, Italy; ³ ENEA, Dip. Innovazione, C. R. Frascati, Italy.
16:00	Break		
Session 5: Processing	16:30	5.1	(Invited) Processing of Diamond by Laser Beam Irradiation Masanori Yoshikawa, Tokyo Institute of Technology, Tokyo, Japan
	17:00	5.2	(Invited) CVD Diamond TEM Sample Preparation by Laser Machining <u>J.E. Butler</u> , D.J. Vestyck, Jr. A. Gilmore, J.W. Steeds, Naval Research Laboratory, Washington DC, USA
	17:30	5.3	Structure and Electronic Properties of Laser-Ablated Diamond Film Surface <u>S.M. Pimenov</u> , E.N. Loubnin, G.A. Shafeev, E.D. Obratsova, A.V. Karabutov, V.V. Kononenko and V.I. Konov, General Physics Institute, Moscow, RUSSIA
	17:50	5.4	Diamond film field electron emission enhancement by pulsed laser post-growth treatment in boron/nitrogen containing gases. V. Ageev, V. Konov, <u>M. Ugarov</u> , E. Loubnin, S. Pimenov, and S. Karabutov, General Physics Institute, Moscow, RUSSIA
19:00	Dinner		

Wednesday, 8 October 1997

Session 6: <i>Applications</i>	09:00	6.1	(Invited) Diamond Photodetectors for Laser based Applications <u>R. Jackman</u> , <i>University College London, UK</i>
	09:30	6.2	(Invited) Applications of diamonds in quantum electronics: review and perspectives. <u>V. Mironov</u> , <i>YGEER&D CNIGRI, "ALROSA" Co., Mirny, Yakutia, RUSSIA.</i>
	10:00	6.3	CVD Diamond Wires and Tips: Growth and Characterization <u>C. Manfredotti</u> ¹ , <u>F. Fizzotti</u> ¹ , <u>A. Lo Giudice</u> ¹ , <u>G. Mucera</u> ¹ , <u>P. Polesello</u> ¹ , <u>E. Vittone</u> ¹ , <u>G. Mariotto</u> ² , <u>C. Vinegoni</u> ² , <u>E. Cazzanelli</u> ³ , <u>N.V. Suetin</u> ⁴ , <u>Y.A. Mankelevich</u> ⁴ , ¹ <i>Universita' di Torino, Dipartimento di Fisica Sperimentale, INFN-Sezione di Torino, INFN-Unita' di Torino Universita', Torino, Italy,</i> ² <i>Universita' di Trento, Dipartimento di Fisica, INFN-Unita' di Trento, Povo (TN), Italy,</i> ³ <i>Universita' della Calabria, Dipartimento di Fisica, Arcavacata di Rende, Italy,</i> ⁴ <i>Moscow State University, Nuclear Physics Institute, Moscow, Russia</i>
	10:20	6.4	Optical characterization of graphitized layers in ion-implanted diamond. <u>R.A.Khmelnitskiy</u> , <u>V.A.Dravin</u> , <u>S.D.Tkachenko</u> , <u>A.A.Gippius</u> , <u>P.N.Lebedev</u> <i>Physical Institute of the Academy of Sciences of Russia, Moscow, Russia</i>
10:40	Break		
Session 7: <i>Thermal properties</i>	11:10	7.1	Spatial Distribution of Thermal Conductivity of Diamond Wafers as Measured by Laser Flash Technique <u>V. Ralchenko</u> ¹ , <u>A. Vlasov</u> ¹ , <u>I. Vlasov</u> ¹ , <u>B. Zubov</u> ¹ , <u>A. Nikitin</u> ¹ , <u>A. Khomich</u> ² , ¹ <i>General Physics Institute, Moscow, Russia,</i> ² <i>Institute of radio Electronics, Moscow, RUSSIA</i>
	11:30	7.2	Acoustic phonons generation in diamond by laser excitation of buried implanted layer <u>T.I.Galkina</u> , <u>A.Yu.Klokov</u> , <u>R.A.Khmelnitskii</u> , <u>A.I.Sharkov</u> , <u>V.A.Dravin</u> , <u>A.A.Gippius</u> , <u>P.N.Lebedev</u> <i>Physical Institute of the Academy of Sciences of Russia, Moscow, Russia</i>
	11:50	7.3	Measurements of Thermal Properties of Diamond Films at High Temperatures <u>V.I. Konov</u> ¹ , <u>S.V. Garnov</u> ¹ , <u>O.G. Tsarkova</u> ¹ , <u>V.G. Ralchenko</u> ¹ , <u>F. Dausinger</u> ² , ¹ <i>General Physics Institute, Moscow, RUSSIA,</i> ² <i>IFSW, Stuttgart, Germany</i>
	12:10	7.4	The Mechanisms of Phonon Scattering in Microcrystalline Diamond Films. <u>V.B.Efimov</u> , <u>L.P.Mezhov-Deglin</u> , <i>Institute of Solid State Physics RAS, Chernogolovka, Moscow distr., Russia</i>
13:00	Lunch		
14:30	City sightseeing tours. Technical visit to SIA «Phonon».		
19:00	Dinner		

Thursday, 9 October 1997

Session 8: <i>Characterization</i> Chair:	09:00	8.1	Using Raman Spectroscopy for 3-D Mapping of Stress in CVD Diamond <i>I.I. Vlasov, and V.G. Ralchenko, General Physics Institute, Moscow, Russia</i>
	09:20	8.2	Role of Different Impurities in Natural Diamond Genesis <i>M. Kh. Ashurov, D.S. Gafitulina, Institute of Nuclear Physics of Uzbek Academy of Sci., Tashkent, UZBEKISTAN</i>
	09:40	8.3	Concentrated Solid Solutions and Dissolution of Diamond and Cubic Boron Nitride <i>M.S. Saidov¹, M. Kh. Ashurov², ¹Physical-Technical Institute of Uzbek Academy of Sciences, Tashkent, Uzbekistan, 'Phonon' Scientific Industrial Association, Tashkent, Uzbekistan</i>
	10:00	8.4	Optical Anisotropy of Natural Diamond Crystals <i>S.V. Sofroneev, and V.P. Mironov, Yakutia State Univ., Mirny, Russia</i>
10:20	Break		
Session 9: <i>Processing</i> cont'd Chair:	10:50	9.1	Diamond Surface Microstructuring by Laser Ablation at Different Wavelengths <i>T. Kononenko, S.V. Garnov, V.G. Ralchenko, I.I. Vlasov, V.I. Konov, General Physics Institute, Moscow, Russia</i>
	11:10	9.2	Laser - Assisted Etching of CVD Diamond Films in Air and in Liquid Media <i>G.A. Shafeev, General Physics Institute, Moscow, Russia</i>
	11:30	9.3	Optical Properties of Laser-modified Diamond Surface <i>A.V. Khomich¹, V.V. Kononenko², S.M. Pimenov², V.I. Konov², S. Gloor³, W. Luthy³, H.P. Weber³, ¹Institute of Radio Eng. & Electronics, RAS, Moscow, Russia, ²General Physics Institute, RAS, Moscow, Russia, ³Institute of Applied Physics, University of Bern, Switzerland</i>
	11:50	9.4	Oxygen-Assisted Laser Cutting and Drilling of CVD Diamond Plates <i>V.V. Migulin¹, V.G. Ralchenko¹, Y-J Baik², ¹General Physics Institute, Moscow, Russia, ²KIST, Seoul, Korea</i>
13:00	Lunch		
19:00	Banquet		

ABSTRACTS

Precision Shaping of a Diamond Surface by Using an Interferometrically Controlled Laser-Ablation Method

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The present paper describes a material processing technique that may be used to precision-shape the surface of a diamond (and possibly other) substrate by ablating the diamond surface using a raster scanned high intensity UV laser beam which is under interferometric control in real time.

A project was initiated to experimentally explore the feasibility of this concept and to demonstrate capabilities (and limitations) of this novel process. This effort was carried out as an international project with participation and technical contributions both from the United States (Rockwell-Rocketdyne) and from Russia (General Physics Institute)

Preparing of optical surfaces by polishing always entails two tasks.

1. Shaping the surface
2. Smoothing ("buffing") the optical surface

In most cases - in conventional polishing - these two tasks are fulfilled simultaneously. In most polishing tasks the desired shape of the optical surface is either flat or spherical (maybe cylindrical)

When the surface shape that needs to be made is arbitrary, or when the optical component to be made (mirror, window) is thin, it is difficult to achieve the desired shape of the optical surface by using conventional polishing methods. When the choice of material is diamond, its hardness further enhances the difficulties associated with production. When the diamond material is polycrystalline CVD diamond in most cases, ordinary polishing in general will not result in high quality optical surfaces.

The presently described diamond surface processing technique consists of three steps.

1. Preparation of the rough CVD diamond surface (smoothing)
The purpose of this first step is to prepare the surface to make it possible to interrogate it interferometrically during the second (laser ablation) step of the process
2. UV Laser Diamond Surface Ablation. In this second phase of the process the "high spots" on the surface are removed. After completion of this second step of the process, the surface shape will be very close to the final, desired shape (flat, aspheric)
3. Ion Beam Assisted Polishing will be used in the final, third step of this process to super polish the surface. The IBAP technique smoothes the surface without altering its shape

The paper will discuss details of these steps of the process.

Experimental results, presented at the conference will show that the present approach is practical on flat surfaces, and also, it appears, that it can be extended to more complex, non-flat surfaces.

Some interesting (and important) new applications, fabrication of various diamond optical and other components that become possible by use of this process will be discussed.

CO₂ Laser Driven Plasma CVD of Diamond and Boron Nitride Films

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The advantages of laser driven plasma CVD for high rate and high gas pressure synthesis of diamond and other materials are discussed. The choice of CO₂ laser (wavelength $\lambda=10.6 \mu\text{m}$) as a single energy source for this purpose is justified. Radiation parameters needed for plasma production and maintenance are given.

The experiments with pulsed plasma (TEA CO₂ laser pulse duration 1 μs , energy 0.5 J and repetition rate 50 Hz) resulted in deposition of hexagonal BN films on silicon from N₂ : BCl₃ :Ar mixture at pressure 150-500 Torr.

It was found that steady-state laser plasmotron can deposit high quality diamond films in air. Ignition and sustaining of plasma in CH₄ :H₂ : noble gas mixture, exhausting into ambient atmosphere over substrate, was performed by 2.5 kW mean power continuous wave CO₂-laser.

This work was supported by Russian and German Ministries of Science and Technology, DiaGasCrown Co., CRDF Grant N 2293

IN SITU OPTICAL INVESTIGATION OF DIAMOND THIN FILM GROWTH

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Real-time monochromatic and spectroscopic optical measurements have been performed in-situ during diamond thin film syntheses on silicon substrates by HFCVD.

Prior to the deposition, Si substrates were either untreated or treated with diamond paste. During the syntheses, the temperature of the tungsten filament was kept to 2200 °C, while the substrate temperature could be varied from 600 to 1000 °C by heating from the rear. The reactive gas consisted in a .5 - 2 vol. % dilution of methane in hydrogen.

The monochromatic measurements used a He-Ne laser radiation ($\lambda_0 = 633 \text{ nm}$) focused on the substrate with an incidence angle θ_i ($\theta_i = 30\text{-}80^\circ$) and with the electric field parallel to the substrate. The scattered light intensity was detected either with a photodiode or with a photodiode array placed. The angle of detection of the scattered light was varied from $\theta_d = 0$ to 30° . The spectroscopic measurements were performed with a deuterium lamp ($\lambda = 200\text{-}450 \text{ nm}$). The incident light was focused on the substrate with a 60° incidence angle and with the electric field in the plane of incidence. The reflected light was detected with a dispersive monochromator equipped with an Optical Multichannel Analyser using CCD detectors. A computer recorded the reflectivity $R_t(\lambda)$ at time t and calculated the differential reflectivity between t and $t + \Delta t$:

$$[\Delta R/R]_{t,\Delta t}(\lambda) = [R_{t+\Delta t}(\lambda) - R_t(\lambda)] / R_t(\lambda)$$

The development of the optical measurements at $\lambda_0 = 633 \text{ nm}$ with deposition time is predominantly governed by light scattering by transparent diamond crystals. In particular, the beginning of the diamond growth is characterised by a strong increase of the scattered light intensity. Modelization of the optical response has allowed us to relate the time development of the scattered light intensity and its spatial distribution to characteristics of the diamond growth kinetics.

The wavelength range of the spectroscopic measurements has been chosen to get information on the nature of the deposited carbon. As a matter of fact, diamond and graphite have very different optical properties. Diamond is an insulator with an indirect optical band gap at 226 nm, graphite is a semi-metal and has a strong interband transition around 270 nm. It has been observed that the diamond crystal growth is always preceded by an incubation period during which the time development of the spectroscopic optical measurements evidence absorption and roughness changes due to competition between the deposition of a disordered graphite layer and its etching by atomic hydrogen.

CHEMICAL VAPOR DEPOSITION OF DIAMOND FILMS ON NONUNIFORMLY HEATED SUBSTRATES

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Abstract

To observe the effect of temperature on the processes polycrystalline diamond films were grown on the nonuniformly heated substrates by hot filament chemical vapor deposition technique using methanol and hydrogen gas mixture in quartz reactor. To provide nonuniformity of substrate temperature molybdenum pedestal was placed on the quartz tube, which removed heat from the substrate. p-type (111) and (100) silicon n-type (0001) and (0001) 6H silicon carbide wafers were used as substrate. The form of the area of the deposited diamond films was dependent on the diameter of the quartz tube. Polycrystalline diamond films with grain size of 1-3 micron were deposited. An applicability of diamond pyramid hardness (microhardness) tester for the preliminary examination of the diamond films is shown. Scanning electron micrographs and Raman spectrum of some films are presented.

LASER ABLATION DEPOSITION OF CRYSTALLINE CARBON NITRIDE FILMS

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The most important development in hard materials of the last years has been on diamond synthesis and processing. Laser deposition of diamond coatings is now a current practice. Taking into account this success, it seems difficult to find a new material which could reasonably compete with diamond. Nevertheless, when it was proposed by Liu and Cohen that a covalently bound carbon nitride (β - C_3N_4) could have characteristics comparable or even better than those of diamond, many efforts were undertaken to synthesize this new material. After a decade of trials carbon nitride has not yet been synthesized in stoichiometric phase. Despite the disappointment, researches are pursued and carbon nitride films, with composition CN_x ($x < 1$) are being prepared by using different techniques in order to study formation processes and film characteristics.

We deposited carbon nitride films on $\langle 111 \rangle$ Si substrates by XeCl excimer laser ablation of graphite in low pressure (1-50 Pa) N_2 atmosphere at laser fluences of 12 and 16 J/cm^2 . Substrates were at room temperature. Many different diagnostic techniques (SEM, EDS, RBS, XPS, XRD, TEM) were used to characterize the deposited films. Films results plane and well adherent to their substrate. N/C atomic ratios up to 0.7 were inferred from RBS measurements. Nitrogen concentration in the deposited layers increases with increasing ambient pressure and laser fluence. XPS investigations indicate two different bonding states of nitrogen atoms, bound to sp^2 -coordinated C atoms and to sp^3 -coordinated C atoms. XRD and TEM analyses point to an oriented microcrystalline structure of the films. Quite large crystals, with an ellipsoidal basis, are grown on the substrate. The major axis of the ellipses ranges between 2 and 15 μm . Electron diffraction studies indicate that the crystals, which seem to exhibit a diamond-like structure, grew almost epitaxially on the $\langle 111 \rangle$ Si substrate. Crystals could be a new CN_x phase or a N-doped diamond phase.

LASER STIMULATION OF DIAMOND GROWTH FROM COMPRESSED GRAPHITE

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The new method of diamond growth from graphite stimulated by laser emission in high-pressure camera is considered. A pulsed-periodic laser emission falls onto the diamond-graphite interface through one of the transparent walls of the camera. The camera, which is a type of a diamond anvil, keeps the pressure above 20 GPa, and the laser emission is heating a very thin graphite skin-layer up to the temperatures from 1000 to 4000 K, and this is sufficient to transform the graphite into the diamond under such conditions. Since the temperature gradients in the skin-layer are large, and the diamond heat conductivity is high, there takes place an anomalously fast cooling of the layer transforming it into the diamond transparent for the laser emission. When the heated layer is cooled and transformed into the diamond layer, the process can be repeated for another layer, and etc.

The photochemical mechanism of the graphite-diamond transition for UV emission is also considered, and the velocity of the wave connected with this transition is estimated.

A series of experiments has been undertaken on the quasistatic compression of the graphite and boron nitride in the diamond anvils, and their heating by high-power laser pulses. As the pressure reaches ~300 kbar and temperature achieves ~2000 K one could observe transformation of the hexagonal phase into a transparent cubic one. The performed experiments confirm a feasibility of a new method (see A.G.Molchanov, V.B.Rozanov, Patent N 95109547, 10.04.1996, Russia) of the diamond production from the graphite in the compressed state under laser heating.

QQC's Laser-Based Technology for Depositing Adherent Coatings on Engineering Tools

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Advances in laser technology has enabled industry to incorporate lasers as manufacturing tools in production. Laser cutting, drilling, welding and stereolithography applications are widely known and accepted methods for product manufacturing. The QQC technology core program includes use of laser technology which enables adherent coatings for applications driven, material synthesis and cost effective flexible product manufacturing. The presentation will highlight some of the potential and current capabilities for surface enhancement for the Diamond Coatings market.

Deposition and laser damage tests of DLC coatings on quartz optical fibers and plates.

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We report on deposition and laser damage tests of DLC coatings on silica plates and tip of 0.4 mm diameter fibers. The carbon films were produced by three techniques: (i) pulsed CO₂ laser sputtering of glassy carbon targets in high vacuum; (ii) monoenergetic carbon ion beam deposition; and (iii) R.F. plasma deposition in benzene. Raman spectroscopy, ellipsometry and scratch tests were used to characterize structure, optical constants n and k , and adhesion of the films. The 20 ns pulses of a Q-switched YAG:Nd laser emitted at 1.06 μm were used to determine the laser damage threshold fluence, W_d , of the films. The R.F. plasma deposited coatings have demonstrated the highest values of $W_d=18-22 \text{ J/cm}^2$. A combination of small thickness (150-200 Å), relatively low absorption ($k=0.10-0.15$), and good adhesion were the key to the success for these films. In spite of lower absorption the a-C films deposited by ion beam technique showed poorer resistance to laser shots because of insufficient adhesion. The a-C films produced by CO₂ laser sputtering have shown the very low damage thresholds ($W_d= 0.65 \text{ J/cm}^2$) because of high absorption ($k=0.6-0.8$). Attempts to produce polycrystalline diamond films on silica fibers are also described.

The Synthesis of Carbyne from Amorphous Linear-Chain Carbon and Pyrographite

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Two carbon materials after the powerful laser influence were studied. The first material was 10 micron film of the amorphous linear chain carbon. The film was prepared by method of ion assisted deposition in Ar atmosphere. The second material was pyrolytic graphite. The samples were irradiated by a 1.06 micron wave-length Nd laser in vacuum 0.3 Pa. The energy of the laser pulse was - 70 J, the duration 580 ps and intensity - 440 GW/cm².

After the experiments the samples were examined by means of transmission electron microscopy and Raman spectroscopy. The formation of carbyne crystals with lattice parameters "a" 0.516 and 0.533 nm were detected in the shocked samples. A small amount of nanodiamond was detected, too. An interesting feature is the formation of gross carbyne crystals (of about 10 microns) in pyrographite. Raman spectra of both recovered materials exhibit strong peaks

at frequencies corresponding to the oscillations of carbon atoms in linear chain structures.

Electron diffraction data were used for crystal potential computation. The results of the computation confirm that carbon chains are packed into hexagonal close packed structure.

RESONANCE ENHANCED MULTIPHOTON IONISATION PROBING OF HYDROGEN ATOMS IN A DIAMOND HOT FILAMENT CVD REACTOR

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Attention is being focused ever more closely on the detailed gas phase chemistry that occurs during diamond chemical vapour deposition (CVD). Many early experiments concentrated on the detection of stable gas phase species, either in the gas mixture exhausting from the reactor or, in more elaborate experiments, in the CVD chamber itself, in the vicinity of the substrate upon which deposition was occurring. Stable species investigated in situ include CH₄ and C₂H₂ (detected, for example, by direct IR absorption and mass spectrometry) and H₂ (monitored via coherent anti-Stokes Raman spectroscopy (CARS)). Laser techniques like CARS can offer several important advantages, e.g. they can offer an unobtrusive, spatially localised measure both of the local gas temperature and of the concentration of the particular species being probed.

Any detailed understanding of diamond growth mechanisms require similarly detailed, spatially resolved information concerning the transient atomic and radical species, and the way in which their concentrations vary with process conditions. Pivotal amongst these are H atoms and small carbon containing species, most notably methyl (CH₃) radicals. Optical diagnostics applied to the measurement of CH₃ radicals in diamond CVD environments include infrared (IR), ultraviolet (UV) and vacuum UV absorption, resonance enhanced multiphoton ionisation (REMPI) spectroscopy and, most recently, cavity ring down spectroscopy (CRDS).

H atoms are also crucial in most diamond CVD environments. They not only drive most of the gas phase chemistry, creating reactive carbon containing radicals from the stable hydrocarbon feedstock gas, but also fulfil a number of key functions at the growing surface. Crucial amongst these are: preferential etching of any non-diamond deposits, termination of 'dangling bonds' at the growing surface thereby preventing reconstruction to non-diamond carbon, and the creation (by abstraction of a surface terminating H atom) of the vacant sites necessary for further growth. Optical techniques used to estimate H atom concentration profiles in diamond CVD reactors have included LIF measurements of the $n=3 \rightarrow n=2$ Balmer-alpha emission following $n=3 \leftarrow n=1$ two photon excitation, 3+1 REMPI via the $n=2$ state and in situ third harmonic generation (THG).

This contribution will focus on our current experimental programme involving use of 2+1 REMPI at 243.1 nm to detect H atoms in a purpose designed and built hot filament reactor for diamond CVD. Strengths and limitations of this and the various alternative H atom detection methods will be summarised, before presentation of a number of representative results illustrating: (i) gas temperature profiles within the reactor (by measurement and analysis of the H atom Doppler profiles), (ii) H atom concentrations as a function of position within the reactor, and (iii) the effect of trace additives (e.g. N₂, Cl₂) on the local H atom concentrations.

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Three-dimensional reconstruction of methyl density in a HFCVD reactor from CRDS experiments.

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The methyl radical is of a primary importance for diamond chemical vapor deposition. Recently new diagnostics [1] for the methyl based on the cavity ring-down spectroscopy (CRDS) technique has been developed. This CRDS is a highly sensitive absorption spectroscopy that determines the absolute absorbance of an excimer-laser-pumped dye laser (Lambda-Physik) pulse passing through a sample. New measurements of the absolute methyl concentration based on the CH_3 absorption cross-section at 213.9 nm have been presented in [1]. Developed three dimensional (3D) model [2] of a hot-filament CVD reactor is used to interpret these measurements of methyl radical profiles and reactor parameters dependencies of CH_3 .

The model consists of three blocks, that describe gas-phase processes (heat and mass transfer, chemical kinetics), gas-surface processes at the substrate (diamond growth mechanisms) and the processes of a reactive mixture activation (gas heating, catalytic hydrogen dissociation at the filament). In the first block the set of conservation equations for mass, momentum, energy and species concentrations was numerically solved taking into account the diffusion and thermodiffusion processes and detailed C/H chemistry and thermochemistry. Reactions of hydrocarbons, atomic and molecular hydrogen with a solid are considered in the second block. In the third block the rate of hydrogen catalytic dissociation at the filament is determined by different methods. Transport equations with the initial and boundary conditions, thermal and caloric equations of state are numerically integrated until steady state regime is reached. As a result, spatial distribution of the gas temperature, flow field, species concentrations and growth rates are obtained.

Without artificial assumptions it is problematically to obtain good correlation of experimental and calculated results using 1D or 2D models. 3D effects - heat and species transfer in lateral direction (and in filament direction if the filament and/or substrate lengths are comparable with the filament-substrate gap and/or the substrate width) are very important. 3D model calculations show that species concentrations are non-uniform in filament directions and CRDS method gives the methyl concentrations averaged over this direction. The appropriate integrally averaged CH_3 concentrations obtained using the 3D model are good agreed with experimental data. By contrast, the methyl density calculated using the 2D model significantly overestimates the experimental data in the off-filament regions.

[1] E.H. Wahl, T.G. Owano, C.H. Kruger et al, *Diamond and Rel. Mater.*, 5 (1996) 373.

[2] Y.A. Mankelevich, A.T. Rakhimov, N.V. Suetin, *Diamond and Rel. Mater.* (submitted).

RAMAN SPECTROSCOPY FOR IN-SITU STUDY OF DIAMOND GROWTH IN DC DISCHARGE PLASMA CVD REACTOR

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Raman scattering is known to be very informative for study of carbon materials including diamond films grown by chemical vapor deposition (CVD). Apparently, there is no alternative method for monitoring the growth of diamond films during CVD process. We report here a real in-situ analysis of the growth process of diamond films in d.c. plasma glow discharge reactor.

Raman spectra measured during CVD diamond growing at various process parameters allow to monitor the temperature of growing film, stresses in the film, and evolution of the film structure, including sp²/sp³ carbon ratio, diamond grains size and structure perfection.

The feasibility of in-situ Raman scattering diagnostics for monitoring the diamond growth gives the effective instrument for optimization of CVD process conditions. Also, this allows to study the fundamental processes of carbon phases formation and their modification, during the growth, on the substrate-plasma or/and the film-plasma interfaces.

Use of Laser spectroscopies for the study of a diamond deposition Microwave Plasma assisted CVD Reactor

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The work presented aims at understanding the role of nitrogen coupled to other deposition parameters on the diamond films quality, microstructure and morphology. In particular, we bring informations which allow to clarify the formation of <100> texture diamond films associated to a (100) morphology.

We have used Laser induced Raman scattering and Photoluminescence spectroscopies as well as SEM analysis for characterizing the diamond films. We have used two photon laser induced fluorescence and emission spectroscopies to characterize the plasma gaseous phase, in particular we focused our analysis on measurements of hydrogen-atom densities.

Although nitrogen addition in the plasma phase was always seen to lead to the development of the <100> texture, we show that its action on the films morphology is strongly related to the H-atom density. As the H-atom density controls the stability of the (111) faces versus secondary nucleation, for percentage of methane up to 6 %, low H-atom density leads in presence of nitrogen to a (100) morphology while high H-atom density leads to a (111) morphology of the films.

During this study, we have also confirmed the results presented by Bergman et al (1) who reported that the 2 eV broad luminescence band of nitrogen containing center involves highly dispersed like amorphous non diamond phases.

(1) L. Bergman, M. T. Mc Lure, J. T. Glass, R. J. Nemanich, The origin of broad band luminescence and the effect of nitrogen doping on the optical properties of diamond films, J. Appl. Phys. 76, issue n°5, 3020-27 (1994)

Diamond : a material for laser spectroscopy

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Diamond polycrystalline films synthesised by chemical vapour deposition (CVD) techniques [1,2] present inherent favourable properties such as hardness, transparency from the far IR to the UV (for IIa type diamond), thermal diffusivity, as well as high Young's modulus. Their physical characteristics make them attractive for laser spectroscopy from the far IR region to the XUV region.

The use of thin films of diamond has been investigated in various applications in the far IR region, where they combine transparency as well as ability to resist to high-flux laser beams. With use of a multikilowatt cw CO₂ laser, it was demonstrated recently [3] that the damage threshold is reached at a fluence of 5 kW/cm². Even higher values could be achieved with pulsed lasers. Moreover, when the film thickness is comparable with or below the laser wavelength, diamond film operates as a Fabry-Perot cavity whatever the incidence angle is. Their polarisation properties are enhanced when the thickness (1-2 μm) is an odd multiple of the quarter-wavelength. With a set of 4 parallel and non-optimised in thickness films at Brewster angle, it has been possible to build a high-efficiency polariser in the 10 μm spectral region giving an extinction ratio better than 1:1000 for the S polarisation [3].

In the deep UV ($\lambda < 225$ nm) and XUV spectral regions the physical and electrical properties of diamond are of interest for the fabrication of fast resistive photoconductors with response time in the 100 ps range. Such detectors, blind to visible light, can be used to measure the intensity and the temporal shape of pulsed VUV radiation. It is of special interest for the characterisation of coherent light produced by harmonic generation or four-wave mixing in a gas. Because nonlinear processes have conversion efficiencies as low as 10⁻³ down to 10⁻⁶, it is necessary for precise VUV measurements to strongly reduce the signal contribution of the intense visible light of the pump laser. A diamond detector composed of a self-supported film 2x2 mm² (180 μm thick) with 2 coplanar electrical contacts [4] has been used to measure with excellent precision the intensity and the shape of VUV laser pulses at 125 nm [5]. Such photodetector could also be used for the characterisation of soft X-ray (≤ 3 keV) pulses.

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- [2] F. Foulon, T. Pochet, E. Gheeraert and A. Deneuille, *IEEE, Trans. Nuc. Sci.* 41 (1994) 927
- [3] C. Chardonnet, V. Bernard, C. Daussy, A. Gicquel and E. Anger, *App. Opt.*, 35 (1996) 6692
- [4] F.Foulon, P. Bergonzo, C. Jany, A. Gicquel, T. Pochet, *Nuc. Instrum. Meth.*, A380 (1996) 42.
- [5] L. Museur, W.Q. Zheng, A. Kanaev and M.C. Castex, *IEEE Sel. Top QE* 1, 900 (1995)

LASERSPECTROSCOPIC STUDY OF DEFECTS IN HPHT DIAMONDS

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Keywords: HPHT synthetic diamonds, Ni-impurities, optical spectroscopy, photochromism

Spectroscopic properties of nickel- and nitrogen-doped HPHT diamonds have been investigated with the aim to establish 1) nature and properties of the aggregate defects regarding the possibilities of using such diamonds as active media in solid-state lasers and 2) photochromic properties of defects to use them in optoelectrical applications.

The crystals grown by BARS technology in the Fe-Ni-C system [1] were subjected to various treatments such as post-growth annealing at temperatures as high as 2000°C and irradiation with high-energy electrons or neutrons with subsequent annealing.

In addition to the S2, S3 and N-V defects our spectroscopic measurements revealed an abundance of spectral lines partly belonging to Ni - N aggregates and showing a rich defect content of the samples. Systematic low-temperature high-resolution spectra of transmission and photoluminescence were measured and the dependence of the lines on the conditions of preparation, excitation wavelength and temperature was investigated. Kinetic parameters of luminescence were measured. Both very fast (ns) and slow lifetimes (ms) were found in the sample the first being characteristic to the nitrogen-related defects in diamond and the second to the nickel-related centres.

We have also investigated photochromic properties of some defects, increasing and decreasing the number of defects responsible for the spectral lines at 546 and 552 nm. Analysis of the kinetics showed that the destruction of the defects with resonant 546 nm photons is a two-photon process but generation of the defects by 441.6 nm photons is a one-photon process. Photoionisation of Ni followed by charge transfer is proposed to be the mechanism responsible for the phototransformation. A tentative scheme of electronic energy levels is presented. Spectrally selective outbleaching in the 546 nm lines has been demonstrated.

1. V.Nadolinny, A. Yelisseyev, *Diamond and Related Materials* **3** (1994) 1196.

Laser-Induced Luminescence Study of CVD Diamond Films with Different Microstructures.

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Recent works on the photoluminescence (PL) of Diamond films show a noticeable dependence on growth methods and deposition parameters. Such a dependence appears to be related to the defected polycrystalline structure of the material and to the presence of impurities and non-diamond phases. Moreover PL spectra strongly depend on excitation energy, particularly in the subgap spectral region, where we are able to probe not only different defect centres but also different micro-environments of the same center. In this paper we summarize the main results achieved in our laboratories during an extensive study of such topics. PL emission and excitation spectra of diamond films grown on silicon by different techniques (Hot Filament CVD, Microwave Plasma-Enhanced CVD and DC Arc-jet) are obtained at RT, liquid N₂ and He temperatures, using laser sources in the range 450-650 nm. In highly-oriented diamond films PL spectra are characterized by sharp vibronic lines mainly involving nitrogen impurities, such as N-V (1.945 eV) and N-V-V (2.154 eV) centres. When diamond films are grown on pre-treated silicon substrates a characteristic vibronic emission appears, peaked around 1.68 eV. Even at relatively low resolution such emission shows an excitation-dependent asymmetrical lineshape which can be decomposed into two components, at 1.673 and 1.681 eV, related to defect centres involving carbon vacancies and silicon-vacancy complexes, respectively. The two components exhibit very similar excitation spectra, with a sharp resonance around 1.9 eV (second excited electronic level) but their relative weights show a strong dependence on both film depth and intergrain position, as revealed by micro-PL measurements. In randomly oriented polycrystalline regions PL spectra are dominated by a characteristic broad band centered between 1.5 and 2.0 eV, whose shape and position are practically independent on the growth method but strongly dependent on excitation energy. This behaviour can be explained by a continuous distribution of gap states, able to trap photogenerated electrons and holes and allowing a two-center radiative recombination. Further information on the presence and distribution of non-diamond phases is obtained by micro-Raman measurements at room temperature, which are also sensible to transverse and lateral stress distribution. Correlation between PL and Raman data are presented and discussed for several diamond microstructures.

PROCESSING OF DIAMOND BY LASER BEAM IRRADIATION

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Abstract

YAG and ArF excimer laser beams, of which wavelengths are 1.06 μm and 193 nm respectively, have been applied to processing of a variety of diamonds. Cutting and smoothing of natural, CVD and sintered diamonds have been performed. CVD diamond films were prepared by arc discharge plasma jet CVD and microwave plasma CVD, and sintered diamonds contain metallic or ceramic binder have been used.

Fundamental processes of diamond cutting and smoothing with YAG and ArF excimer laser have been investigated using natural single crystal and CVD diamonds in various atmospheres changing laser irradiation conditions such as average power, energy density, pulse repetition rate and laser scanning times. Moreover, laser processing mechanisms of diamond have been discussed on basis of the observations of groove formation and by the spectroscopic analysis of the emission during irradiation.

Cutting of natural and CVD diamond with YAG laser proceeds at higher peak power that occurs at lower pulse repetition rates. smooth surfaces are obtained by excimer laser irradiation at the incident angle of 80° . In the cases of the processing with YAG laser, the effect of local heating by laser beam irradiation mainly assists the diamond processing, and diamond appears to be removed after graphitization and oxidization following vaporization in the atmosphere contains oxygen. The temperature measurement was carried out at backside of irradiation surface, and increase of temperature when YAG laser beam was irradiated was larger than that when excimer laser was irradiated. On the contrary, the detection of C, C₂, C⁺, C₂⁺, O₂ and CO from the emission at the irradiation area with ArF excimer laser beam suggests that processing partly proceeds by the separation of carbon atoms from the surface of diamond after breaking bonds between carbon atoms caused by laser beam. Cutting of sintered diamond with metallic binder was difficult because metallic binder remains in the groove while ceramic binder was easily removed.

Cutting and smoothing techniques using laser beams have been applied to surface planing, chip preparation and edge formation of CVD diamond and forming of curved surface of sintered diamond. Surface planing was carried out of directing the YAG laser beam parallel to the surface of diamond films and diamond chips were prepared by the combination of cutting and surface planing techniques. Sharp edge was formed between the surfaces which cut by laser beam and mechanically polished. Round nose was formed by gradually rotating the sintered diamond following YAG laser beam irradiation.

CVD Diamond TEM Sample Preparation by Laser Machining

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The defect structure of diamond films grown by microwave plasma chemical vapor deposition (CVD) is studied by using laser machining to slice thin sections from free standing films ca. 200 microns thick. This technique has enabled the examination of the defects at the nucleation and growth surface of optically clear CVD diamond films. A cw Q-switched Nd³⁺/YAG laser was used to slice 1 to 15 micron thick wedges, ca. 3mm in length from 150 to 220 micron thick diamond films. The edges of the as cut wedges were thin enough for examination by transmission electron microscopy (TEM). Subsequent ion milling was used to thin the edges further. Remarkably low defect densities are observed at the growth surface after 150 microns of growth.

STRUCTURE AND ELECTRONIC PROPERTIES OF LASER-ABLATED DIAMOND FILM SURFACE

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It is well known that laser ablation of diamond films is accompanied by diamond-to-graphitic conversion, leading to the formation of a thin graphitized layer at the diamond surface. Basic consequences of the laser-induced surface modification of the diamond films are that the laser-ablated surface becomes highly conductive and its structure, according to Raman spectroscopy analysis, is that of glassy carbon (nanocrystalline graphite). However, the electronic structure of the laser-ablated diamond was found to be modified and different from the valence band structure of other carbon materials, in particular, of glassy carbon and highly-oriented pyrolytic graphite. A specific feature of the modification of the valence band structure is its broadening due to the appearance of the occupied electronic states in the gap.

In this work, the valence band modifications of the laser-ablated diamond surface are considered in relation to i) laser activation of diamond for electroless selective-area metal deposition, and ii) enhanced field electron emission from the laser-graphitized diamond films.

Experimental studies of selective-area metallization of diamond films are presented with emphasis on i) laser activation of diamond for electroless metal plating, ii) electroless metal deposition onto the activated surface areas, and iii) diamond growth onto the metal-patterned diamond films, encapsulating metal patterns into diamond.

Field electron emission properties of the original and laser-graphitized diamond films are studied and compared with those of glassy carbon and HOPG, demonstrating lower emission fields and higher current stability for the laser-graphitized diamond. Application of the laser ablation technique for fabricating microstructures such as micropyrarnid arrays at the diamond film surface is demonstrated, and preliminary results on the field emission testing of the produced one-dimensional microstructures are presented.

The work was supported in part by the International Science and Technology Center under the Project #198.

.Diamond film field electron emission enhancement by pulsed laser post-growth treatment in boron/nitrogen containing gases.

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As a result of pulsed ArF laser irradiation of the surface of nano-crystalline diamond films in borazine ($B_3N_3H_6$) and ammonia (NH_3) atmospheres a multifold reduction of threshold electric field of field electron emission was observed. To study the structure and composition of surface layer the methods of Auger electron spectroscopy and Raman spectroscopy were used. It was found that the laser processing produced the interplanar penetration of boron and nitrogen atoms into the diamond film to the depth of 50 nm, the incorporated atoms forming chemical bonds of type B-C-N, and after the irradiation in ammonia - C-N bonds of mixed sp^2/sp^3 type. It is established that the change of emission characteristics of diamond films is not connected with surface graphitization or formation of bulk defects, and the laser irradiation in the vacuum causes no essential effect on the emission threshold.

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Diamond Photodetectors for Laser based Applications

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The wide band gap of diamond and its high electrical resistivity suggest that it is an ideal material for the fabrication of deep UV photodetectors which are 'blind' to visible light. Diamond devices should also have high damage thresholds when used in UV laser applications. The emergence of high quality thin film diamond, grown by CVD techniques, has enabled such devices to become commercially accessible. However, the optoelectronic properties of diamond, even in its natural form, are far from ideal; early attempts to fabricate UV photodetectors were disappointing with high dark currents, low sensitivity to UV light and a significant response to visible light all being encountered. Recently we have been able to modify the optically active defect structure of CVD grown diamond using various gas treatments that have enabled us to demonstrate truly visible blind detector characteristics along with low dark currents. Devices with photoconductive gains of up to 1 million have been designed and fabricated. The speed of response of these devices can be several orders better than early devices.

This paper will consider the designs and gas treatments used to control the extrinsic photoconductive response and carrier lifetimes within CVD diamond and present information on the UV photodetector performance levels that have been achieved. The use of these devices within UV laser based applications will be discussed.

APPLICATIONS OF DIAMONDS IN QUANTUM ELECTRONICS: REVIEW AND PERSPECTIVES.

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Creation of laser media based on the materials with high thermal conductivity, hardness and photochemical stability of color centers, with the possibility to create of them in high concentration is a current problems. Diamond are unrivaled in these characteristics. Wide electronic-vibrational systems in absorption and luminescence allows to relies four-level pumping scheme, the turning of generation over wide bandwidth and the use of the crystals as the material for passive laser Q-switchers. Theoretical analyze shown, the diamond is perspective for application in laser thecnics.

Since 1978, when the first communication about perspectives of diamond application in laser technics appeared, the next result are important.

1. Stimulated emission from H3 centers with turning over 500-600 nm region (USA and Russia).
2. Stimulated emission from H2 centers with turning over 800-1000 nm region (Japan).
3. Investigations possibility of using N3 centers (USA).
4. Raman laser based on diamond (Japan).
5. Investigation of nonlinear absorption of H3, H4, and GR1 centers (Russia).
6. Prototypes of passive Q-switchers for argon laser based on diamond with H3 and H4 centers (Russia).
7. Prototypes of passive Q-switcher for ruby laser based on diamond with GR1 centers (Russia).
8. Number preparation methods of laser media based on diamond (Japan, Russia, USA).

The result are modest. The nearest perspectives are stimulated radiation by 640 centers with turning over 650 -750 nm region, wide bandwidth tunable radiation by A-luminescence band, UV stimulated radiation at 230-240 nm.

In quantum electronics we have the same problems, like semiconductors one. The technology not perfect because we have not enough theoretical background. We have to investigate the electronic and optic processes in diamond, as for as the processes of creation, perturbation and destruction of defects in diamond, complete system of energetic levels and so on.

Other reason - we have not good enough materials with satisfaction size. 15 -20 years later we would have synthetic diamonds with enough size and excellent optic quality and return to technological and production problems.

CVD Diamond Wires and Tips: Growth and Characterization

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We present a systematic study of the growth of polycrystalline diamond thin films on W wires (50-300 micrometer diameter) and tips by hot filament assisted chemical vapour deposition (HFCVD).

We carry out correlations between Scanning Electron Microscopy (SEM) observations and micro-Raman (micro-R) spectra, while varying different growth parameters (wire and tip diameter, CH₄/H₂ ratio, etc.), in order to establish relationships between growth rate, quality of the films and growth conditions.

We have also simulated the growth process using the developed three-dimensional model of a HFCVD reactor. In the model full transport equations are solved with regard to the detailed gas-phase chemistry and surface processes on the filament and substrate. The calculated and experimental results are compared.

Keywords: diamond thin films, HFCVD, Scanning Electron Microscopy, micro-Raman spectroscopy, growth model

OPTICAL CHARACTERIZATION OF GRAPHITIZED LAYERS IN ION-IMPLANTED DIAMOND.

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Due to metastability of diamond it tends to transform to graphite if lattice damage density exceeds some critical value. In this case a sufficient number of diamond sp^3 bonds are broken which is a prerequisite for transformation (enhanced by heating) into a graphite phase with sp^2 bonds. The possibility to graphitize selected areas of diamond subjected to radiation damage provides an additional degree of freedom in the development of diamond based electronic devices. One can think of built-in graphite resistors, capacitors, connections between elements of circuits etc.

In this paper we present the data of optical characterization of graphitized layers formed in diamond by ion implantation and annealing. Samples of natural diamond were bombarded at room temperature by He^+ ions with the energy of 350 keV and fluence of the order of $10^{16} cm^{-2}$ and subsequently annealed in vacuum at $1400^\circ C$. Starting from the critical fluence of $2.8 \times 10^{16} cm^{-2}$ the absorbing and reflecting buried graphitized layers were formed.

In the first series of experiments we performed optical measurements taking into account the absorption in the buried damaged layer and interference in the part of the crystal between the surface and the buried layer to obtain the data on the depth and the thickness of the layers as well as their conductivity at optical frequencies. It was shown that within the range of 360 keV He^+ ions fluences $(3.0 \div 4.5) \cdot 10^{16} cm^{-2}$ the depth and the thickness of the graphitized layer can be varied within $(726 \div 677) nm$ and $(70 \div 168) nm$ respectively. The optical parameters of the buried absorbing layer at $\lambda = 700 nm$ were found to be: the refractive index $n = 2.21 \pm 0.06$ and the extinction coefficient $k = 0.70 \pm 0.03$ which are close to those of dispersed graphite ($n = 2.05$, $k = 0.66$).

In the second series of experiments we performed cathodoluminescence analysis of diamond samples containing several areas implanted with 350 keV He^+ ions with fluences below and above the threshold of formation of the graphitized layer. Monitoring the spectra of cathodoluminescence and the intensity of lines of the well-documented optical centres at different points of the sample (outside the implanted area, within the areas implanted with fluences below and above the threshold) we found evidence of vacancy migration over macroscopic distances ($\sim 150 \mu$). It was found also that the conditions of formation and/or properties of the optical centres in the area with the buried graphite layer are different from those in the area without the layer. This difference might be due to the fact that the density of graphite is lower than that of diamond, which is bound to produce considerable tension in the part of the crystal between the surface and the buried layer.

Spatial Distribution of Thermal Conductivity of Diamond Wafers as Measured by Laser Flash Technique

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Thermal conductivity perpendicular to diamond film surface was measured using laser flash technique (LFT). Polycrystalline diamond wafers of 100-500 microns thickness and 57 mm diameter were produced in microwave plasma at different deposition conditions. Thermal conductivity (k) was determined from heat propagation time across the wafer after short (8 ns) pulse of a Nd:YAG laser absorbed at sample surface. Distributions of k along wafer radius were measured with 1 mm spatial resolution and correlated to nitrogen content, Raman diamond peak width and amorphous carbon presence in the material. The best K values of 18 W/cmK were recorded for selected samples. The data obtained with LFT are in agreement with results determined by classical method of stationary thermal flux. A relationship between thermal conductivity and deposition regimes is discussed.

ACOUSTIC PHONONS GENERATION IN DIAMOND BY LASER EXCITATION OF BURIED IMPLANTED LAYER

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Heat transfer in dielectrics and semiconductors at low (liquid helium) temperatures is performed by acoustic phonons. At present, there are practically no data on the evolution of acoustic phonon system in diamond, in spite of the fact that the problem of heat transfer is of importance for applications.

In this paper we present the data on the development of a specific version of the so-called heat pulse technique as applied to diamond. In general heat pulse technique implies generation of acoustic phonons near the surface of a solid and the analysis of their propagation in the crystal using some phonon-sensitive detector. Generation of phonons is conveniently achieved using pulsed laser whose quanta are absorbed at or near the surface either by a metal film deposited on a sample or by sample itself. In the case of diamond (with the band gap of 5.5 eV) the latter version requires a powerful UV source and special optics which presents some difficulties.

We have developed a new phonon generation method — the laser excitation of buried implanted layer which is not transparent for the nitrogen laser light with the wavelength 337 nm. At the same time, this layer is 'built-in' into the diamond matrix and, consequently, has no thermal boundary resistance. This layer was produced by implantation of the He^+ ions with energy 300 keV and with a dose of $4.5 \cdot 10^{16} \text{ cm}^{-2}$.

The detector response which was obtained in this experiment on natural IIa type diamond was extremely narrow with FWHM 25-30 ns and was independent of the excitation level. This result gives an evidence of the ideal acoustic match of the implanted layer and the diamond matrix. Comparison of the experimental responses with the data of calculations allowed us to determine the phonon scattering constant $2 \cdot 10^{-44} \text{ s}^{-3}$, which presumably corresponds to the phonon scattering by isotopes.

Heat transfer in the sample of synthetic diamond ($N_{\text{nit}} \sim 10^{20} \text{ cm}^{-3}$) have also been measured, with the broader responses than for the pure IIa diamond. Phonon scattering constant was found to be 3 times that of natural IIa diamond which is probably due to the contribution of scattering by impurities.

Measurements of Thermal Properties of Diamond Films at High Temperatures

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Express laser technique for high temperature measurements of optical (reflectivity R_λ and transmission J_λ) and thermophysical (heat capacity C_p) of materials has been developed and applied to CVD diamond plates.

Continuous wave Nd:YAG laser ($\lambda=1,06 \mu$) with mean power 150W is used both for heating and probing the samples. The irradiated plates have diameter 3-3,5 mm, close to focused beam diameter, and thickness 0,2-0,4 mm and are suspended on two tungsten wires inside photometric sphere. Transmitted through the sample light is collected by polished metal tube attached to its rear side. Typical heating time is a few seconds and maximum temperature 300⁰C. The irradiated surface brightness temperature T_b at wavelength $\lambda_p=0,914\mu$ was controlled by fast optical pyrometer. Simultaneous monitoring of T_b and sample optical properties at $\lambda \approx \lambda_p$ permitted to determine real temperature dependence $R(T)$ and $J(T)$ for $T > 800^0$ C. In the described experimental conditions diamond plates are thermally thin and insulated that allowed with chopped beam to obtain C_p values by means of $T(t)$ and $dT/dt(t)$ measurements.

CVD diamond samples of different quality were investigated by the developed technique. Correlation of the observed behavior of $R(T)$ and $J(T)$ with material graphitization is discussed.

The Mechanisms of Phonon Scattering in Microcrystalline Diamond Films.

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The investigation of the thermal conductivity of diamond films gives us a very important information about mechanisms of heat transport. On the one hand, the knowledge of absolute values of the thermal conductivity is the main characteristic for practical application of diamond films as a high heat transmission substrate, on the other hand, this material is very convenient model system with very high Debye temperature ($\theta_D \approx 2200$ K), and room temperature is low temperature for diamond in comparison with any another materials. The phonon wave length is of the order of ten parameter of lattice at room temperature and of the order of 1000 Å at helium temperatures.

We experimentally have studied the thermal conductivity of the free-standing microcrystalline diamond films in temperature range 8-350 K. It was found at room temperature the thermal conductivity of the best samples is limited by phonon-phonon scattering with loss of pulse (Umklapp processes). Phonon mean free path l_p increases with cooling of the sample. The thermal conductivity of these samples are close to the thermal conductivity of diamond single crystals.

At low temperatures the phonon-boundary scattering process stays dominate and l_p limits by crystalline size. For worse samples the phonon-defects scattering defines the phonon mean free path and thermal conductivity at room temperatures.

At liquid nitrogen and below phonons begin penetrate through crystalline boundaries and l_p increases with decreasing the temperature of the samples.

Using Raman Spectroscopy for 3-D Mapping of Stress in CVD

Diamond

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Evolution of local intrinsic stress in chemical vapour deposition (CVD) diamond films was studied by confocal micro-Raman spectroscopy. For this purpose the series of high quality diamond films were grown by microwave plasma enhanced CVD. Both film-forming and isolated individual crystals of 20 to 200 nm size and of different growth orientations were analysed. Stress mapping was held both on the film surfaces and in a bulk of the films. For stress measurements across the film thickness mechanical polishing of the films were used. In surface analysis the Raman probing with 2 μm spatial resolution was not enough to detect smooth changes of stress for the films of lower than 100 nm thickness. For the thicker films Raman diamond lines observed were generally fitted by two narrow Lorentzian profile, e.i. the stress magnitude was close to constant in the probing volume. In some cases the two components can be completely resolved in succession by polarization analysis. In bulk analysis a resolution of the Raman probing degenerates, but general tendencies of stress behaviour can be traced.

It was found that both compressive and tensile stresses exist only simultaneously within individual crystal. Local stress region as shown to increase with film thickness. It can be explained by increasing of growth sectors with highly different content of defects under film deposition. Maximum stress fluctuation detected came up to 9 GPa, according to our estimations.

ROLE OF DIFFERENT IMPURITIES IN NATURAL DIAMOND GENESIS

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Key words: impurity, distribution, autoradiography, growth.

Evidence of growth kinetics and debate genesis questions of natural is available only an indirect way with decoding the paragenetic information contained in crystals, in particular, impurity composition of inner part. Growth mechanism of crystal, impurity concentration and their distribution between different phases are depending on metastable level. Therefore impurity distribution can be the indicator of unequal condition level.

On the base activation autoradiography method including digital treatment it was investigated the impurity distribution in natural diamonds. Identification of radionuclides and the qualitative evaluation of their contents was conducted by gamma-spectrum of specimens irradiated by neutrons. The impurity distributions have been studied on $\langle 100 \rangle$ and $\langle 110 \rangle$ lamellar cut from crystals of an octahedral, rhombododecahedral and cubic habit having a zonal texture. It were established the different distributions of several impurities (Mn, Na, Cu, Co, Fe, Si, Al, Ni).

Topography of impurity distributions was changed on dependence from crystal habit and impurity nature.

These phenomenons may be realized on the base of combining of Cahn-Routburd growth theory with Prigogine-like synergetic idea. The type of crystallization mechanisms depends of relation between crystallization moving force and value of combine parametr, depending of boundary wide. A lot of regimes of crystallization was discussed.

CONCENTRATED SOLID SOLUTIONS AND DISSOLUTION OF DIAMOND AND CUBIC BORON NITRIDE

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Abstract

The solubility in the multicomponent systems is discussed. Considering the molecular elements (C₂, B₂, etc.) and some combinations of elements not shown on the traditional phase diagrams as the new chemical compounds the conditions of the formation of their continuous substitutional solid solutions with the single covalent bond are suggested. Using the valences and covalent radii of B, C, N, Be, O, Al, Si and P the possibility of the formation of concentrated and continuous solid solutions, based on diamond and cubic boron nitride is substantiated. To back up such a possibility the brief review of the experimental data on the (IV₂)_x(III-V)_{1-x} and (IV₂)_x(II-VI)_{1-x} continuous solid solutions are presented. An increase of hardness of diamond and cubic boron nitride is expected as a result of the formation of their concentrated solid solutions. Taking into account the advantages of thinning of CVD diamond plates with a molten alloys and the idea on substitutional and interstitial liquid solutions for the processing of the polycrystalline CVD diamond plates by the effective dissolution a number of molten alloys are predicted.

CVD diamond film processing by nanosecond pulses of IR-UV spectral range

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Lasers can be effectively used for diamond processing including cutting, drilling, patterning and polishing of diamond films. A choice of an optimum laser system for a particular application should be based on a comparative experimental study of laser-diamond interaction under variation of main laser radiation parameters, in particular, wavelength.

Ablation of diamond films grown by microwave plasma CVD upon irradiation by nanosecond (5-9 ns) pulses at three different wavelengths 1078, 539 and 270 nm at laser fluence in the range of $1 \div 10^3$ J/cm² was investigated. A Nd:YAP laser system operated at first, second and fourth harmonics was used in the experiments. Ablation rates measured for shallow craters and through holes with the aspect ratio up to 5 were compared. The reduction of the etch rate in the process of crater deepening was ascribed to the effect of laser-plasma interaction inside a deep channel. The ablation rate was found to be wavelength-independent, that was explained by surface blackening caused by amorphization/graphitization as confirmed by Raman analysis. The maximum etch rate approached 600 nm/pulse.

The possibility to produce holes and trenches of high aspect ratio, as well as 3D structures (pockets) has been demonstrated. The regular structures with a period of 3-4 μ m have been obtained at 1078 nm wavelength by means of a specially designed optical system providing tight focusing of laser beam with about 2 μ m beam waist value. The effect of the ablation start delay observed for IR radiation at low energy densities is discussed.

LASER - ASSISTED ETCHING OF DIAMONDS IN AIR AND IN LIQUID MEDIA

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Etching with the help of a copper vapor laser (wavelength of 510 nm, pulse duration of 10 ns, pulse repetition rate of 8 kHz) of diamond polycrystalline CVD films is studied in various surrounding media (air, H₂O, (CH₃)₂SO). Diamond samples are virtually transparent at this wavelength, and the coupling of laser radiation to diamond is due to the formation of a thin graphitized layer at the diamond surface. The etching rate in liquid media is slightly higher than in air at otherwise equal conditions and is as high as 50 μm/s under the etching with a scanning laser beam. The diamond surface etched in air and in liquid environment is characterized with Raman spectroscopy, SEM, and AFM. The diamond surface etched in liquids is virtually free of the glassy carbon layer. Electroless deposition of metals (Cu, Ni, Pt) on the laser-etched features is studied to compare the catalytic activity of the diamond surface etched in air with that etched in liquids. Possible mechanisms are discussed responsible for the observed difference both in the structure of the etched area and in the electroless metal deposition onto the surface etched in various media (air or liquids).

Optical Properties of Laser-modified Diamond Surface.

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Laser polishing of chemical vapor-deposited (CVD) diamond film is a promising technique in view of thermal, optical and tribological applications. Among the variety of lasers, two types of pulsed lasers are widely used for diamond film polishing. The first group includes excimer lasers which operate at wavelengths from 193 to 351 nm. The use of the excimer lasers takes advantage of the high value of light absorption in diamond, while the pulse repetition rate is not high (typically up to 200 pulses/sec). The second group of lasers includes those operating in visible and near-IR spectral regions (wavelengths from 500 to 1000 nm) with a very high repetition rate of 1-10 kHz.

In this paper we used a copper vapor laser (CVL) (510 nm, 20 ns pulse duration, 8 kHz repetition rate) for laser polishing of high-quality diamond films of 350 μm thick. The angle of a laser beam incidence with respect to the surface normal was 70-80°. The diamond films were placed on an computer-controlled X-Y translation stage to provide the beam scanning over the sample surface. Optical spectroscopy measurements were carried out using IR and UV-VIS "Specord" spectrometers in two spectral ranges 0.185-0.9 μm and 2.5-50 μm .

The surface relief of the as-grown diamond films was greatly smoothed with a scanning beam. The initial surface roughness of 20-30 μm was reduced to 0.1-0.3 μm . Thus polished surface areas of about 4x4 mm² were examined with the UV-VIS and IR optical spectrometers. As the laser processing of diamond involves two-steps: the transformation of diamond to graphite in the first few pulses followed by the sublimation of graphite with the additional laser pulses, a removal of the laser-graphitized layer on the diamond surface is needed. For this purpose, annealing in ambient oxygen was used. The annealing (oxidation) experiments were performed at 200 - 650 C in air (for 0.5 hour for each temperature). Optical spectra were taken from the samples after each successive annealing procedure. We observed a non-monotonous modification of the optical spectrum depending on the annealing temperature and regimes of the laser polishing. At the first step (200-400 C) the upper graphite layer was evacuated from the diamond surface, while the 20-50 nm thick CVL-modified surface layer with the characteristic 255 nm-centered absorption band in the UV spectra demonstrated high oxidation stability. The physical mechanisms for the formation of laser-modified layers on diamond are discussed.

Oxygen-Assisted Laser Cutting and Drilling of CVD Diamond Plates

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A parametric study of cutting and drilling of thick (up to 0.5 mm) diamond films with a Nd:YAG laser was performed. The high quality wafers of 2.5 inch diameter were produced using microwave plasma CVD technique. Cutting rate as function of laser energy, beam scanning velocity, number of scans were determined. An acceleration of ablation rate and a reduction of carbon redeposition effects were observed when an oxygen jet was directed to laser-diamond interaction zone. Machining the films covered with Ti-Pt-Au metallization layer showed results similar to those for virgin diamond surface. Microcutting and patterning of diamond plates with a copper-vapor-laser are also demonstrated.

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