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Optymalizacja procesu syntezy jednofazowych materiałów LiFePO₄ o nanometrycznych rozmiarach ziaren

ME 2016, 44, 3, s. 4

Próbki materiału LiFePO₄ przygotowano zmodyfikowaną metodą zol - żel. Otrzymany kserożel został roztarty w moździerzu i kalcynowany w piecu rurowym w atmosferze ochronnej, w przepływie azotu. Główny cel pracy jakim było obniżenie temperatury i czasu trwania procesu, został osiągnięty. Potwierdzono, że materiał ten składa się tylko z tryfilitowej fazy LiFePO₄. Dowiedziono, że węgiel obecny w próbce, pochodzący z rozkładu pirolitycznego wyjściowych soli organicznych nie wpływa na formowanie się fazy krystalicznei.

Badanie metodami wysokorozdzielczej dyfraktometrii rentgenowskiej monokryształów ZnO bombardowanych jonami Ar

ME 2016, 44, 3, s. 9

Za pomocą wysokorozdzielczej dyfraktometrii rentgenow-skiej (HRXRD) badano tetragonalizację komórki elementarnej monokryształu tlenku cynku powstałą pod wpływem bombardowania jonami Ar. Objętościowe monokryształy ZnO o orientacji (00-1) były bombardowane jonami o energii 300 keV, w przedziale dawek od 1 x 10¹⁴ cm⁻² do 4×10^{16} cm⁻². Zarejestrowano profile dyfrakcyjne otrzymane metodą radialnego skanowania 2 Teta/Omega, w otoczeniu węzła 00·4, sieci odwrotnej ZnO i w oparciu o założenia dynamicznej teorii dyfrakcji promieniowania rentgenowskiego w ujęciu Darwina, wykonano ich symulacje numeryczne. Na tej podstawie określono, w zależności od dawki, profil zmiany odległości płaszczyzn prostopadłych do osi c monokryształu ZnO. Stwierdzono, że dla niskich dawek, w ściśle określonej objętości kryształu, powstaje dodatnie odkształcenie równoległe do osi c, wraz ze wzrostem dawki jonów to odkształcenie wzrasta, a po osiągnięciu pewnej krytycznej wartości ulega nasyceniu. To prowadzi do wniosku, że w implantowanej objętości kryształu powstaje wówczas odkształcenie plastyczne.

Rezonator z poprzeczną falą powierzchniową na krysztale tantalanu litu do zastosowań w czujnikach lepkości i temperatury cieczy

ME 2016, 44, 3, s. 17

Celem pracy były obliczenia i pomiary parametrów poprzecznej akustycznej fali powierzchniowej w rezonatorze na krysztale tantalanu litu o orientacji 36°YX oraz pomiary lepkości i temperatury cieczy. Odpromieniowanie energii akustycznej od powierzchni do objętości kryształu zamodelowano wprowadzając współczynnik tłumienia fali różny od zera. Przyjęto najnowsze dostępne w literaturze stałe materiałowe tantalanu litu. Obliczono prędkość i współczynnik sprzężenia elektromechanicznego, współczynnik odbicia od pojedynczej elektrody, współczynnik tłumienia przy powierzchni swobodnej i metalizowanej oraz współczynnik anizotropii. Z wykorzystaniem rezonatora synchronicznego wykonano pomiary trzech pierwszych wielkości. Uzyskano dobrą zgodność pomiarów z obliczeniami. Skonstruowano dwukanałowy rezonator czuły na iloczyn lepkości i gęstości cieczy osadzonej na metalizowanej powierzchni międzyprzetwornikowej. Zbadano temperaturowy współczynnik częstotliwości (TWCz) kanału przeznaczonego do pomiaru temperatury.

THE ARTICLES ABSTRACTS ME 2016 - 44 - 3

Optimization of synthesis of single phase nanostructured LiFePO₄ materials *ME 2016, 44, 3, p. 4*

2010, 44, *S*, *p*. 4

LiFePO₄ samples were first prepared by a modified sol - gel process and then the resulting LiFePO₄ xerogel was ground and calcined in a tube furnace in an inert atmosphere in nitrogen flow. The main goal of this research work which was lowering the temperature and the time of synthesis of LiFePO₄ was achieved. It was confirmed that the material contains only a LiFePO₄ triphylite phase and that the presence of carbon resulting from pyrolysis of initial carbonaceous reagents does not affect the crystalline structure of the material.

HRXRD study of ZnO single crystals bombarded with Ar ions

ME 2016, 44, 3, p. 9

High resolution X-ray diffraction methods (HRXRD) were used to study the tetragonalization of a unit cell in a zinc oxide single crystal resulting from the Ar-ion bombardment. Bulk ZnO (00-1) single crystals were bombarded with ions with the energy of 300 keV and a dose range between 1×10^{14} cm⁻² and 4×10^{16} cm⁻². Diffraction profiles, obtained by radial 2Theta/Omega scans in the vicinity of the 00.4 ZnO reciprocal space node were measured and fitted to the curves calculated by means of a computer program based on the Darwin's dynamical theory of X-ray diffraction. On the basis of these numerical simulations, the profile of the interplanar spacing between planes perpendicular to the c axis of the ZnO single crystal were determined as a function of the Ar ion dose. It was found that positive deformation parallel to the c-axis appeared for the low doses in the bombarded crystal volume. When the dose is increased this deformation gets pronounced, and after reaching a certain critical value, it becomes saturated. This observation leads to the conclusion that the plastic deformation appears in the implanted volume of the crystal.

Resonator with transverse surface wave on lithium tantalate crystal for applications in viscosity and temperature sensors

ME 2016, 44, 3, p. 17

The purpose of this work was to calculate and measure transverse surface acoustic wave resonators on 36°YX oriented lithium tantalate crystal as well as to measure of viscosity and temperature of liquids. An attenuation coefficient was used to model the leak of acoustic energy from surface into bulk of the crystal. The latest materials constants were used. Velocity, electromechanical coupling coefficient, reflection coefficient, attenuation coefficient under free and metallized surface, anisotropy coefficient were calculated, the first three of which were measured using synchronous resonator. A good agreement between measurements and calculations were obtained. Double-channel resonator was sensitive to viscosity and density multiplication product of liquid deposited on the metallized area between transducers. The temperature coefficient of frequency (TCF) of the temperature cure channel was measured.

Optimization of synthesis of single phase nanostructured LiFePO₄ materials

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Abstract: LiFePO₄ samples were first prepared by a modified sol - gel process and then the resulting LiFePO₄ xerogel was ground and calcined in a tube furnace in an inert atmosphere in nitrogen flow. The main goal of this research work which was lowering the temperature and the time of synthesis of LiFePO₄ was achieved. It was confirmed that the material contains only a LiFePO₄ triphylite phase and that the presence of carbon resulting from pyrolysis of initial carbonaceous reagents does not affect the crystalline structure of the material.

Key words: lithium iron phosphates, olivines, nanocrystalline materials, sol-gel preparation, thermal analysis, crystal structure

Optymalizacja procesu syntezy jednofazowych materiałów LiFePO₄ o nanometrycznych rozmiarach ziaren

Streszczenie: Próbki materiału LiFePO₄ przygotowano zmodyfikowaną metodą zol - żel. Otrzymany kserożel został roztarty w moździerzu i kalcynowany w piecu rurowym w atmosferze ochronnej, w przepływie azotu. Główny cel pracy jakim było obniżenie temperatury i czasu trwania procesu, został osiągnięty. Potwierdzono, że materiał ten składa się tylko z tryfilitowej fazy LiFePO₄. Dowiedziono, że węgiel obecny w próbce, pochodzący z rozkładu pirolitycznego wyjściowych soli organicznych nie wpływa na formowanie się fazy krystalicznej.

Słowa kluczowe: fosforan litowo - żelazowy, oliwiny, materiały nanokrystaliczne, proces zol - żel, analiza termiczna, struktura krystaliczna

1. Introduction

The LiMXO₄ type compounds (M = Fe, Co, Ni; X = S, P, As, Mo, W) represent an intensively studied group of cathode materials for reversible lithium ion cells [1]. In 1997 the lithium iron phosphate LiFePO, with the olivine structure was recognized by Goodenough [2] as a prospective cathode material for Li-ion cells. Further studies confirmed the important advantages of LiFePO₄ over LiCoO₂ [3] used in commercial batteries. Those advantages include better safety, lower risk of explosion on overcharging, better thermal stability or lower cost of raw materials [4 - 5]. Unfortunately LiFePO, has a major drawback — poor electronic conductivity, 10⁻⁹ Scm⁻¹ at 20°C [6]. Many research works have been conducted to improve the conductivity of this material by several methods such as: aliovalent doping [7 - 8], preparation of composites with carbon [9], Fe₂P [10] or other additives [11], and modifications of grains morphology [12]. In the course of these studies it was shown that satisfactory performance of LiFePO₄ - olivine materials in batteries could be achieved if the average size of LiFePO4 particles goes down to below 100 nm [13]. It was demonstrated that discharging

capacity drops with the increased particle sizes from 165 mAh/g for ~30-50 nm diameter to 72 mAh/g for 500 nm and bigger particles [13]. This feature also affects the conductivity in terms of the effective electrode resistance.

These days syntheses use either solid-state reaction or hydrothermal/solvothermal processes. In the first case the synthesis is typically conducted at temperatures above 700°C and may involve the synthesis from molten salts [14]. The advantages of the second example regard control of the homogeneity and the average crystallite size [15]. The conventional hydrothermal process requires a reaction time in range 5 - 12 h [16]. An important issue concerning cathode materials for Li - ion batteries is their cost, which should be as low as possible [17].

The aim of our work was to simplify and reduce the costs of LiFePO₄ preparation by lowering the temperature of the final syntheses and reducing the time of the overall processing. The prepared materials were studied by a number of methods: X-ray diffractometry (XRD), differential scanning calorimetry-thermogravimetry (DSC-TGA), scanning electron microscopy (SEM) and surface area (BET).

2. Experimental

2.1. Materials and synthesis

The material was prepared in accordance with a modified version of the sol-gel recipe described in [18]. We applied standard chemical procedure: organic salts of lithium acetate dihydrate (Sigma Aldrich, pure for analysis) and iron citrate monohydrate (Fluka, pure for analysis), dissolved separately in deionized water, and orthophosphoric acid (POCH, pure for analysis) as initial reagents. After the organic salts had dissolved completely the individual solutions were mixed together and orthophosphoric acid was added. The clear solution was continuously stirred at 80°C for a few hours and then 0.4 M of citric acid (POCH, pure for analysis) was added as complexing agent in the amount of 10 ml per for every 1g of final LiFePO₄. The xerogel which was obtained after the initial evaporation of water was then dried at 150°C in air for 48 h, and finally ground in an agate mortar to a fine powder. The main modification was introduced in the calcination process. During a standard annealing process xerogels are synthesized at 700 - 800°C range for 6 -8 h [19]. In our modified approach the temperature was lowered and the time was shortened to avoid uncontrollable agglomerates formation and to keep crystallites small during the prolonged thermal treatment. The xerogel was annealed for several hours in a steady flow of nitrogen in two stages: first at 300°C and then at 500°C for 5 h. The powder prepared in this way contained some amount of carbon, a residue of the decomposition of the complexing agent and organic salts.

2.2. Characterization

Thermal studies (DSC-TG) were carried out using a NETZSCH STA 449 F1 Jupiter apparatus in the range of 20 - 500°C at a 5°C min⁻¹ heating rate, on 25 mg samples. The phase composition of the samples was examined by powder X-ray diffractometry (XRD) using a Philips X'Pert apparatus equipped with Cu Ka X-ray source with Ni filter $(\lambda = 1.54$ Å). The XRD measurements at a set of temperatures (30 - 800°C) were carried out using an Anton-Paar HTK1200 high-temperature oven chamber. Results were analyzed and confronted with the thermal features seen in DSC-TG traces of the same materials. The morphology of the powders was investigated by scanning electron microscopy (SEM) using a Cross Beam Auriga (Carl Zeiss) setup. Specific surface area was measured using QUADRASORB evoTM Gas Sorption Surface Area based on BET theory [20] at relative pressure conditions $P/P_{o} =$ 0.05 - 0.3, where P – adsorbate saturated vapor pressure.

3. Results and discussion

DSC-TG curves of a xerogel are shown in Fig. 1. Measurements were taken in nitrogen atmosphere to prevent iron oxidation from Fe^{2+} to Fe^{3+} . Up to 350°C it is easy to see a single endothermic peak corresponding to the thermal decomposition of the organic components of citrates and acetates as well as the evaporation of residual water correlated with TG trace. An exothermic doublet above 400°C on DSC curve marks a two step



Fig. 1. Thermogram DSC/TG/DTG of a LiFePO₄ xerogel, heating rate 5°C/min in nitrogen atmosphere. DSC curve shows crystallization process during heat-treatment.

Rys. 1. Termogram DSC/TG/DTG kserożelu LiFePO₄, szybkość grzania 5°C/min w atmosferze azotowej. Krzywa DSC pokazuje proces krystalizacji w czasie obróbki termicznej.



Fig. 2. Series of XRD patterns showing LiFePO₄ triphylite phase formation in function of temperature. The temperature sequence goes from in-situ measurements in nitrogen atmosphere. Eye catching dashed lines of LiFePO₄ reflections.
Rys. 2. Seria dyfraktogramów rentgenowskich XRD pokazujących proces formowania się fazy tryfilitowej w funkcji temperatury. Sygnał XRD zbierano w czasie trwania procesu wygrzewania. Przerywana linią zaznaczono miejsca występowania refleksów braggowskich dla fazy tryfilitowej LFP.



Fig. 3. XRD patterns for LiFePO₄ synthesized in nitrogen atmosphere at 500 and 800°C with indexed Bragg reflections of LiFePO, olivine from ICDD card no. 40 - 1499.

Rys. 3. Dyfraktogramy XRD LiFePO₄ syntetyzowane w temperaturze 500°C i 800°C z zaindeksowanymi refleksami braggowskimi zgodnymi z kartą ICDD nr 40 - 1499.

crystallization process of LiFePO₄ triphylite phase. Further structural investigations (XRD, Fig. 2) showed that a small exothermic feature around 420°C is not correlated with structural changes or formation of an additional phase. The calculated derivative of the original TG curve (DTG) depends on the temperature in an almost identical way as the measured DSC signal. The only difference which can be noted between DSC and DTG is the presence of an exothermic doublet in DSC (in the range of 410 - 450°C) with no effect in DTG trace at the same temperature. The reasons of the presence of such doublet could be assigned to pre-formation of triphylite phase, formation of intermediate composition, such as LiH_2PO_4 [21], or thermal decomposition of lithium acetate [22].

The formation of triphylite phase was investigated by X-ray diffractometry. In-situ observations were conducted at a series of temperatures (300 - 800°C) in nitrogen atmosphere. Before these studies, xerogel was pre-heated in an inert atmosphere up to 300°C in order to perform the pyrolytic decomposition of organic salts and to remove its gaseous products. This temperature selection was based on the analysis of the endothermic features in the DSC curve. Fig. 2. presents a collection of XRD patterns. All Bragg reflections correspond to the orthorhombic LiFePO, triphylite phase (Pnma space group, ICDD card No. 40 -1499) [23]. There are no peaks from unwanted phases like Fe₃P, Fe₂P, Li₃Fe₂(PO₄)₃ or Fe₂O₃. A small visible single peak at ca. 18° corresponds to the sample holder's material. This peak fades as intensity of triphylite phase reflections are increased during the calcination process.

The final high temperature XRD scan was performed at 800°C. After cooling down the last scan was collected at room temperature. The observed series of XRD patterns proved that the material is thermally stable in a wide range of temperatures in an inert atmosphere. More detailed results of studies on crystal structure of samples prepared at 500°C and 800°C are presented in Fig. 3. The positions of the Bragg reflections for both samples are identical, but the reflections for the material prepared at 500°C are much wider and less intense in comparison to



Fig. 4. SEM micrograph of nanostructured LiFePO₄ synthesized at 500°C in N_2 . Clearly visible nanosized hexagonal platelets of LiFePO₄ (white or light grey particles).

Rys. 4. Obraz SEM mikrostruktury LiFePO₄ po syntezie w 500°C w atmosferze azotowej. Widoczne na zdjęciu nanometryczne heksagonalne płytki (białe lub jasnoszare obiekty).

those for the material synthesized at 800°C. An average crystallite sizes estimated by the Scherrer formula [24] were 50 - 60 nm and 10-20 nm for LiFePO₄ calcined at 800°C and 500°C, respectively.

Detailed studies on thermal treatment of xerogel based on XRD and DSC measurements showed a small shift in triphylite formation's temperature. XRD patterns revealed that the main reflections of the LiFePO, phase appeared around 400°C, while with DSC scans the crystallization doublet was recorded at about 420°C. Probably this shift is due to the different heating protocols and rates between DSC and XRD experiments. The heating rate in DSC process was 5°C/min and in various temperature XRD measurements it was around 0.5°C/min. In such case recording of DSC exothermic peak is delayed in time due to the inertness of the sample, which is manifested by an upward temperature shift. In our previous research [18] additional peak in lower temperature was not present in DSC scans because the starting materials used for the sol-gel synthesis were different. As temperature XRD measurements have shown there is no additional phase during heating process in the range of 400 - 450°C. This means that an additional peak in the DSC curve is related to the decomposition of acetates. Longer temperature exposure and the heating time during XRD measurements allowed triphylite phase formation and stabilization at lower temperature. Though One can the peaks visible in XRD patterns correspond to the triphylite phase, not all peaks are present. This may indicate that 400°C is the temperature high enough to initiate the process of crystallization, but too low to complete the phase conversion. Some amount of organic components may still be present in the sample which manifests itself by a relatively high noise to signal ratio.

In addition to the structural analyses, SEM observa-

tions were also conducted to the microstructure. Fig. 4. presents a micrograph of an as-received material synthesized at 500°C with well developed hexagonal platelets of LiFePO₄ [25], of diameters below 100 nm and heights about 15 - 20 nm. Those low values as well as crystallite size estimates from the Scherrer formula (10 - 20 nm), prove that the obtained samples are true nanostructural materials.

The specific surface area of a sample prepared at 500°C determined by the BET method was about $86 \pm 4 \text{ m}^2/\text{g}$, which is considerably higher than the values in range 11- 44 m²/g reported in the literature [26 - 28].

4. Conclusions

The paper presents a modified approach to the preparation of nanostructured LiFePO₄ materials. It was shown that, using a modified sol-gel process and inexpensive reagents, the syntheses of LiFePO₄ olivines can be considerable improved by reducing their temperature from typical 800°C to ca 500°C and by reducing their time from 8 hrs to 5 hrs. As prepared material was nanostructural with particle size below 100 nm, as shown by SEM with crystallite sizes about 10 - 20 nm, calculated by the Scherrer formula. An increased specific surface area and a nanostructural character of the synthesized materials is of great advantageous for their application in lithium-ion batteries. Moreover the introduced synthesis modifications make the whole process more economical.

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HRXRD study of ZnO single crystals bombarded with Ar ions

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Abstract: High resolution X-ray diffraction methods (HRXRD) were used to study the tetragonalization of a unit cell in a zinc oxide single crystal resulting from the Ar-ion bombardment. Bulk ZnO (00.1) single crystals were bombarded with ions with the energy of 300 keV and a dose range between 1 x 10^{14} cm⁻² and 4 x 10^{16} cm⁻². Diffraction profiles, obtained by radial 2Theta/Omega scans in the vicinity of the 00.4 ZnO reciprocal space node were measured and fitted to the curves calculated by means of a computer program based on the Darwin's dynamical theory of X-ray diffraction. On the basis of these numerical simulations, the profile of the interplanar spacing between planes perpendicular to the c axis of the ZnO single crystal were determined as a function of the Ar ion dose. It was found that positive deformation parallel to the c-axis appeared for the low doses in the bombarded crystal volume. When the dose is increased this deformation gets pronounced, and after reaching a certain critical value, it becomes saturated. This observation leads to the conclusion that the plastic deformation appears in the implanted volume of the crystal.

Key words: HRXRD, ZnO monocrystal, ion implantation, radiation defect analysis

Badanie metodami wysokorozdzielczej dyfraktometrii rentgenowskiej monokryształów ZnO bombardowanych jonami Ar

Streszczenie: Za pomocą wysokorozdzielczej dyfraktometrii rentgenowskiej (HRXRD) badano tetragonalizację komórki elementarnej monokryształu tlenku cynku powstałą pod wpływem bombardowania jonami Ar. Objętościowe monokryształy ZnO o orientacji (00·1) były bombardowane jonami o energii 300 keV, w przedziale dawek od 1 x 10¹⁴ cm⁻² do 4 x 10¹⁶ cm⁻². Zarejestrowano profile dyfrakcyjne otrzymane metodą radialnego skanowania 2Teta/Omega, w otoczeniu węzła 00·4, sieci odwrotnej ZnO i w oparciu o założenia dynamicznej teorii dyfrakcji promieniowania rentgenowskiego w ujęciu Darwina, wykonano ich symulacje numeryczne. Na tej podstawie określono, w zależności od dawki, profil zmiany odległości płaszczyzn prostopadłych do osi c monokryształu ZnO. Stwierdzono, że dla niskich dawek, w ściśle określonej objętości kryształu, powstaje dodatnie odkształcenie równoległe do osi c, wraz ze wzrostem dawki jonów to odkształcenie wzrasta, a po osiągnięciu pewnej krytycznej wartości ulega nasyceniu. To prowadzi do wniosku, że w implantowanej objętości kryształu powstaje wówczas odkształcenie plastyczne.

Slowa kluczowe: wysokorozdzielcza dyfrakcja rentgenowska, monokryształ ZnO, implantacja jonów, analiza defektów radiacyjnych

1. Introduction

ZnO is a wide bandgap energy (Eg = 3.37eV) semiconductor. Its most important properties include direct and very high exciton binding energy (60 meV), strong piezoelectric effect, high conductivity, high heat capacity and low thermal expansion coefficient. Due to its wide potential application spectrum in microelectronics, biosensors, spintronics and light sources, ZnO has been the most intensively explored semiconductor material of the last decade [1]. Ion bombardment represents an attractive tool for semiconductor compound processing (doping, isolation etc.). However, a major drawback of this technique is the buildup of lattice disorder due to the ballistic character of this process [2, 4]. Means that in spite of the vast amount of accumulated data, the mechanism of defect buildup in ZnO is not completely elucidated.

Damage accumulation in ion-bombarded compound semiconductors is a consequence of collision damage sequential evolution in extended defects such as dislocations or stacking faults. Our study of GaN [5 - 6] revealed that damage accumulation is a three-step process. The HRXRD analysis indicated that ion bombardment to low doses causes an increase in the c parameter, thus leading to a strain buildup in the implanted region. Once the critical value of the shear stress is reached, plastic deformation due to the dislocation slip appears to take place, and as a result a dislocation tangle is formed. The transition to Stage III – amorphization – takes place at a high impurity concentration and is apparently due to the defect–impurity interaction.

2. Experimental

High-quality commercial [00·1] single ZnO crystals delivered by MaTecK, Germany, were ion-bombarded at the Institute of Electronic Materials Technology (ITME) using the Balzers MBP 202RP ion implanter with 300 keV Ar⁺ ions to doses ranging from 1×10^{14} cm⁻² to 1×10^{16} cm⁻² at room temperature (RT). The structural characteristics of implanted ZnO monocrystals can be determined using



Fig. 1. X-ray diffraction profiles performing 2THETA/OMEGA scans for the virgin ZnO monocrystal implanted with doses ranging from 1×10^{12} cm⁻² to 1×10^{16} cm⁻².

Rys. 1. Rentgenowskie profile dyfrakcyjne otrzymane metodą skanowania 2THETA/OMEGA dla monokryształu ZnO nieimplantowaego, a także implantowanego dawkami od 1 x 10^{12} cm⁻² do 1 x 10^{16} cm⁻².

the non-destructive HRXRD method. To this end, the SmartLab diffractometer equipped with a 9 kW rotating Cu anode (wavelength CuK_{a1} equals 0.15405 nm) was used to perform the X-ray diffraction measurements. The radial 2Theta/Omega diffraction profiles were recorded for the following incident optics settings: cross beam optics CBO unit, Ge(220) x 2 monochromator, open soller slit, and on the receiving side: an open soller slit and soller slit of 5.0 deg. All measured samples were adjusted in such a way that the c-axis was parallel to the φ - axis of the goniometer. So as to obtain radial scans of the (00·4) reciprocal lattice spot of the ZnO monocrystals. The resultant diffraction profiles are presented in Fig. 1.

The influence of implantation on the X-ray diffraction profile is strongly dependent on the ion dose. The shape of the 2Theta/Omega diffraction patterns in the vicinity of the 00·4 reciprocal lattice spot of the implanted ZnO monocrystal, is characterized mainly by the asymmetry that appears on the low-angle side of the afore mentioned node. This asymmetry becomes greater when the dose of Ar ions becomes increased. A relatively high and well-separated peak appears for doses ranging from 1 x 10¹⁴ cm⁻² to 2 x 10¹⁵ cm⁻², on the low-angle side of the 00.4 node while for the highest doses (e.g. 5 x 10^{15} cm⁻² and 1 x 10^{16} cm⁻²) only some oscillations can be observed.

In order to study lattice deformation resulting from ion implantation, the collected experimental data were analyzed by means of computer simulations. The code, based on Darwin's dynamical theory of X-ray diffraction [7 - 8], was developed to perform X-ray diffraction profile simulation. For the purpose of such simulation, a heterostructure is modeled as a stack of parallel atomic planes. For each plane different chemical composition is assumed, which allows modeling graded hetero-interfaces. Based on the assumed chemical composition of the atomic planes, the code calculates the interplanar spacing between succeeding atomic planes and their scattering power. The diffraction profile for a crystal after ion irradiation can be calculated by displacing some of the atoms from their equilibrium positions in the atomic planes, and especially out of their position on the Bragg planes. This results in the modification of the interplanar atomic spacing and planar scattering power profiles [9]. The analysis is performed with the aim to diversify the chemical composition of each atomic plane (or planar scattering power and interplanar spacing) until the best fit between experimental and simulated X-ray diffraction profiles is achieved. The code was tested while working with Al_xGa_(1-x)As/GaAs superlattices to be applied as a Bragg mirror [10].

For the purpose of the simulation, the region of the ZnO monocrystal with the strain induced by ion irradiation was modeled as a stack of parallel layers, perpendicular to the c axis, each of which was 9 nm thick and differed in terms of interplanar spacing and/or planar scattering power. The profile of the interplanar spacing modulation in the growth direction was assumed to reproduce the shape of displaced atom distribution in ion-implanted ZnO [11 - 12]. This distribution was treated as the primary piece of data in X-ray profile calculations, and can be approximated by the Gaussian in the following form:

$$d(\mathbf{x}) = d_0 \left(1 + \mu \exp\left(\frac{-4 \ln 2(x - x_0)^2}{\sigma^2}\right) \right), \qquad (1)$$

where:

d(x) is the interplanar spacing between the (00·4) planes in the strained layer, located at an x distance from the surface, d_0 is the (00·4) interplanar spacing in virgin ZnO, μ is the maximal lattice misfit between the strained layer and virgin ZnO, x_0 is the position of the center of the Gaussian peak, and σ is the full width in the half maximum of the standard distribution.

The fit between the experimental and calculated diffraction profiles was obtained by changing the values of the x_{0} , σ and μ parameters (Fig. 2).

The examples of the best fits between the experimental and calculated diffraction profiles as well as strain profiles are shown in Fig. 3 - 7.



Fig. 2. Graded layer model of the strain distribution in the implanted region of the ZnO monocrystal. **Rys. 2.** Model rozkładu naprężeń w implantowanej objętości monokryształu ZnO.



Fig. 3. X-ray diffraction profiles: experimental (solid) and calculated (dash) for the ZnO monocrystal implanted with the ion dose of 1 x 10¹³ cm². Reflection 00·4, $x_0 = 180$ nm, $\sigma = 30$ nm, $\langle d \rangle = 0,1301666$ nm, $\mu = 0.015365$. **Rys. 3.** Rentgenowskie profile dyfrakcyjne: doświadczalny (ciągły) i obliczony (przerywany) dla monokryształu ZnO implantowanego dawką 1 x 10¹³ cm². Refleks 00·4, $x_0 = 180$ nm, $\sigma = 30$ nm, $\langle d \rangle = 0,1301666$ nm, $\mu = 0,015365$.



Fig. 4. X-ray diffraction profiles: experimental (solid) and calculated (dash) for the ZnO monocrystal implanted with the ion dose of 1 x 10^{14} cm⁻². Reflection 00.4, $x_0=180$ nm, $\sigma = 100$ nm, <d>= 0.1302327 nm, $\mu = 0.024200$. **Rys. 4.** Rentgenowskie profile dyfrakcyjne: doświadczalny (ciągły) i obliczony (przerywany) dla monokryształu ZnO implantowanego dawką 1 x 10^{14} cm⁻². Refleks 00.4, $x_0 = 180$ nm, $\sigma = 100$ nm, <d>= 0.1302327 nm, $\mu = 0.024200$.



Fig. 5. X-ray diffraction profiles: experimental (solid) and calculated (dash) for the ZnO monocrystal implanted with the ion dose of 2 x 10¹⁵ cm⁻². Reflection 00·4, $x_0 = 180$ nm, $\sigma = 140$ nm, $\langle d \rangle = 0.1304943$ nm, $\mu = 0.085291$. **Rys. 5.** Rentgenowskie profile dyfrakcyjne: doświadczalny (ciągły) i obliczony (przerywany) dla monokryształu ZnO implantowanego dawką 2 x 10¹⁵ cm⁻². Refleks 00·4, $x_0 = 180$ nm, $\sigma = 140$ nm, $\langle d \rangle = 0,1304943$ nm, $\mu = 0,085291$.



Fig. 6. X-ray diffraction profiles: experimental (solid) and calculated (dash) for the ZnO monocrystal implanted with the ion dose of 5 x 10¹⁵ cm⁻². Reflection 00·4, x_0 =180 nm, σ = 120 nm, $\langle d \rangle$ = 0.1306206 nm, μ =0.139054. **Rys. 6.** Rentgenowskie profile dyfrakcyjne: doświadczalny (ciągły) i obliczony (przerywany) dla monokryształu ZnO implantowa-



Fig. 7. X-ray diffraction profiles: experimental (solid) and calculated (dash) for the ZnO monocrystal implanted with the ion dose of 1 x 10¹⁶ cm⁻². Reflection 00·4, x_0 =180 nm, σ = 130 nm, <d>= 0.1306401 nm, μ =0.143664. **Rys. 7.** Rentgenowskie profile dyfrakcyjne: doświadczalny (ciągły) i obliczony (przerywany) dla monokryształu ZnO implantowanego dawką 1 x 10¹⁶ cm⁻². Refleks 00·4, x_0 = 180 nm, σ = 130 nm, <d>= 0.1306401 nm, μ = 0.143664.



Fig. 8. Gaussian strain distributions induced in the Ar ion-implanted ZnO monocrystals. Rys. 8. Gaussowski rozkład odkształceń wywołanych w monokrysztale ZnO na skutek implantacji jonów Ar.

Fig. 8 presents the Gaussian strain distributions for which the best fit between the experimental and calculated diffraction profiles was achieved. Each of the presented strain distribution was induced in the ZnO monocrystal through irradiation with different Ar-ion doses.

For doses equal to or higher than 2 x 10^{15} , in order to find a good fit between the calculated and measured X-ray diffraction profiles it was necessary to assume that the planar structure factor of (00·4) planes in the damaged region is reduced in comparison with that of the perfect crystal. It may be explained by the fact that as a result of irradiation, a fraction of the atoms is moved from their positions, out of the Bragg planes and cease to scatter coherently the X-ray photons. Computer calculation of the X-ray diffraction profile is carried out by employing the planar scattering factor, at the same time allowing its modification. In the case of the ZnO monocrystals, the formula describing the planar scattering factor of the (00·4) Bragg planes in the implanted volume of the crystal took the following form:

$$F_{00.4}(x) = \xi(x) (f_{Z_n}(x) + f_0(x)), \qquad (2)$$

where: f_{Zn} - the atomic factor of zinc, f_0 - the atomic factor of oxygen, $(f_{Zn}(x) + f_0(x))$ - the planar scattering factor of the (00·4) Bragg planes in the non-implanted ZnO crystal and $F_{00\cdot4}$ is the planar scattering factor in the implanted ZnO region, as the largest shifts of Zn and O atoms from their Bragg position occupied in the perfect crystal could be expected only in the vicinity of the maximum of the standard strain distribution. The function $\xi(x)$ was defined as:

$$\xi(x) = 1 - \alpha \exp\left(\frac{-4\ln 2(x - x'_0)^2}{\sigma_1^2}\right), \quad \alpha \in [0:1], \quad (3)$$

where parameter α is determined during the search of the best fit between the theoretical and experimental profiles,

 σ_1 is the full width at half maximum and x'_0 is the position of the maximum of the Gaussian function. In this work we assumed an equal reduction of the atomic scattering factors of both oxygen and zinc.

Fig. 9 presents the $\xi(x)$ functions for 2 x 10¹⁵, 5 x 10¹⁵ and 1 x 10¹⁶ cm⁻² ion doses.

A convenient measure of the crystalline order characterization of the implanted ZnO monocrystal is the parameter characterizing a degree of amorphization η , ranging from $\eta = 0$ for the implanted volume in which all atoms are in their correct Bragg position, to $\eta = 1$ for the amorphic material with all atoms moved out of their Bragg positions, and is defined as follows:

$$\eta = \frac{1}{D} \int_{0}^{D} (1 - \xi(x)) \, dx = \frac{\alpha}{D} \int_{0}^{D} \exp\left(\frac{-4 \ln 2(x - x'_{0})^{2}}{\sigma_{1}^{2}}\right) dx, \quad (4)$$

where: η is the degree of amorphization, and *D* denotes the total width of the implanted region.



Fig. 9. $\xi(x)$ functions for 2 x 10¹⁵ cm⁻², 5 x 10¹⁵ cm⁻² and 1 x 10¹⁶ cm⁻² ion doses, obtained to ensure the best fit between the theoretical and experimental diffraction profiles.

Rys. 9. Funkcja $\xi(x)$ dla dawek 2 x 10¹⁵ cm⁻², 5 x 10¹⁵ cm⁻² i 1 x 10¹⁶ cm⁻² otrzymana dla najlepszego dopasowania rentgenowskich profili dyfrakcyjnych doświadczalnych i obliczonych.

lon dose [cm ⁻²]	μ	Average misfit Δa/a [ppm]	Average interplanar spacing [nm]	σ [nm]	σ₁ [nm]	<i>x</i> '₀ [nm]	<i>x</i> ₀ [nm]	α	Degree of amorfization η
5 x 10 ¹¹	0.001906	12	0.1301666	30	-	-	180	0	0
1 x 10 ¹²	0.002151	29	0.1301688	30	-	-	180	0	0
5 x 10 ¹²	0.003457	64	0.1301733	35	-	-	180	0	0
1 x 10 ¹³	0.015365	93	0.1301771	37	-	-	180	0	0
5 x 10 ¹³	0.017669	190	0.1301897	50	-	-	180	0	0
1 x 10 ¹⁴	0.024200	520	0.1302327	100	-	-	180	0	0
1 x 10 ¹⁵	0.059923	2100	0.1304383	160	-	-	180	0	0
2 x 10 ¹⁵	0.085291	2530	0.1304943	140	120	180	180	0.5	0.13
5 x 10 ¹⁵	0.139054	3500	0.1306206	120	140	180	180	0.9	0.24
1 x 10 ¹⁶	0.143664	3650	0.1306401	130	160	180	180	1.0	0.35

Tab. 1. Parameters of strain distribution and $\xi(x)$ function for the ZnO monocrystals implanted to different doses of Ar ions. **Tab. 1.** Parametry rozkładu odkształceń oraz funkcja $\xi(x)$ dla monokryształu ZnO implantowanego kolejnymi dawkami jonów Ar.

The $\alpha = 0.5$ and $x_0 = 180$ nm values mean that in the atomic plane located at the depth of 180 nm at least 50% of atoms were displaced from their regular Bragg lattices sites. For $\alpha = 1$, all atoms from this plane were displaced. In tab. 1, the average strain values calculated for ion doses of 2 x 10¹⁵, 5 x 10¹⁵ cm⁻² and 1 x 10¹⁶ cm⁻² were presented, assuming that amorphization did not occur. Then, these values were overestimated. The same applies to the interplanar spacings.



Fig. 10. The average misfit between the implanted layer and the remainder of the ZnO monocrystal. **Rys. 10.** Srednie niedopasownie sieciowe pomiędzy implantowaną i pozostałą objętością monokryształu ZnO.

In Tab. 1 the main structural parameters are listed, thus yielding the best fit between the experimental and calculated X-ray diffraction profiles.

The average misfit between the implanted layer and the remainder of the ZnO monocrystal is shown in Fig. 10.

Three regions can be distinguished. The first region ranges from 5 x 10^{11} cm⁻² to 5 x 10^{13} cm⁻², the second one from 5 x 10^{13} cm⁻² to 1 x 10^{15} cm⁻², and finally the third one is above 1 x 10^{15} cm⁻². In the first region, the dependence between the ion doses and the average misfit

 $\Delta a/a$ in the whole implanted region can be presented in the following form:

$$\frac{\Delta a}{a} = 60 \log(I) - 690$$

In the second region, the same relation is shown as:

$$\frac{\Delta a}{a} = 1500 \log(I) - 20000$$

There is no linear dependence in the third region.

3. Discussion

Strain development is a vital clue to understanding damage accumulation and its transformation in ZnO. Every displaced atom produces quasi-hydrostatic pressure in the lattice cell. Since the bombarded lattice is constrained by the underlying, undamaged crystal to expand only in a direction perpendicular to the surface, the implanted laver is in the lateral compression and gives the strain distribution. Consequently, the tetragonalization of the lattice cell can be measured by HRXRD. Our study shows the growth of tetragonalization of the ZnO unit cell versus the ion implantation dose. This effect may be created due to the agglomeration of vacancies and interstitial atoms. These processes seem to last until a particular critical stress value is reached before eventually transformation to Stage II takes place. This is typical for plastic deformation. A similar case of transformation was described for GaN, in which the tensile stress was produced by extended defects, also causing the lattice spacing increase (compatible with the Hook's law). Once the yield point had been reached, transformation to Stage II was driven by plastic deformation and the release of stress could be observed [14 - 17]. The resemblance between HRXRD profiles for both materials implies that most likely similar processes occur in ZnO.

4. Conclusions

Damage accumulation in compound single crystals such as some oxides $(SrTiO_3, ZrO_2, MgAl_2O_4)$ or GaN, appears to be a complex, multi-step process [18 - 19]. The key driving force is the elastic strain in the damaged region, which develops in the bombarded areas. It is induced by simple defect agglomeration, resulting in the formation of stacking faults, faulted loops or dislocations. Based on the results described in this paper it can be concluded that the defect behavior in ZnO follows a similar pattern.

Moreover, it has been shown clearly that the damage buildup in compound crystals should be studied using HRXRD analysis of the shift of atoms from their position on the Bragg planes.

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Resonator with transverse surface wave on lithium tantalate crystal for applications in viscosity and temperature sensors

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Abstract: The purpose of this work was to calculate and measure transverse surface acoustic wave resonators on 36°YX oriented lithium tantalate crystal as well as to measure of viscosity and temperature of liquids. An attenuation coefficient was used to model the leak of acoustic energy from surface into bulk of the crystal. The latest materials constants were used. Velocity, electromechanical coupling coefficient, reflection coefficient, attenuation coefficient under free and metallized surface, anisotropy coefficient were calculated, the first three of which were measured using synchronous resonator. A good agreement between measurements and calculations were obtained. Double-channel resonator was sensitive to viscosity and density multiplication product of liquid deposited on the metallized area between transducers. The temperature coefficient of frequency (TCF) of the temperature channel was measured.

Key words: synchronous resonator, surface transverse wave, lithium tantalate, LiTaO₂, viscosity sensor

Rezonator z poprzeczną falą powierzchniową na krysztale tantalanu litu do zastosowań w czujnikach lepkości i temperatury cieczy

Streszczenie: Celem pracy były obliczenia i pomiary parametrów poprzecznej akustycznej fali powierzchniowej w rezonatorze na krysztale tantalanu litu o orientacji 36°YX oraz pomiary lepkości i temperatury cieczy. Odpromieniowanie energii akustycznej od powierzchni do objętości kryształu zamodelowano wprowadzając współczynnik tłumienia fali różny od zera. Przyjęto najnowsze dostępne w literaturze stałe materiałowe tantalanu litu. Obliczono prędkość i współczynnik sprzężenia elektromechanicznego, współczynnik odbicia od pojedynczej elektrody, współczynnik tłumienia przy powierzchni swobodnej i metalizowanej oraz współczynnik anizotropii. Z wykorzystaniem rezonatora synchronicznego wykonano pomiary trzech pierwszych wielkości. Uzyskano dobrą zgodność pomiarów z obliczeniami. Skonstruowano dwukanałowy rezonator czuły na iloczyn lepkości i gęstości cieczy osadzonej na metalizowanej powierzchni międzyprzetwornikowej. Zbadano temperaturowy współczynnik częstotliwości (TWCz) kanału przeznaczonego do pomiaru temperatury.

Slowa kluczowe: rezonator synchroniczny, poprzeczna fala powierzchniowa, tantalan litu, LiTaO₃, czujnik lepkości

1. Introduction

a)

Acoustic waves are differed by vibration character, planes of mechanical displacements symmetry of medium particles and they may appear in various modes. Mechanical displacements of the wave are described by four parameters. These are the three components of mechanical displacements vector: longitudinal u_{1} , transverse horizontal u_{2} ,

transverse vertical u_3 and the electric potential φ (Fig. 1a). The displacements amplitudes depends on the type of wave and the medium in which the wave propagates. In this work we investigated properties of surface acoustic wave with dominating transverse displacement components u_2 (transverse SAW) in lithium tantalate crystal with orientation 36°YX (Fig. 1b) are investigated.



Fig. 1. Components $[u_1, u_2, u_3]$ of particles displacements (a), orientation 36°YX (b), (x_1, x_2, x_3) – coordination system related to wave, (X, Y, Z) – coordination system related to crystal.

Rys. 1. Składowe $[u_1, u_2, u_3]$ przemieszczeń cząstek ośrodka (a), orientacja 36°YX (b), (x_1, x_2, x_3) – układ odniesienia związany z falą, (X, Y, Z) – układ odniesienia związany z kryształem.

2. Calculations of SAW parameters

2.1. Calculation method

Arbitrary wave that propagate in piezoelectric medium fulfils the following equations:

$$c_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_i} + e_{kij} \frac{\partial^2 \varphi}{\partial x_k \partial x_i} = \frac{\partial^2 u_j}{\partial t^2}, \tag{1}$$

$$e_{ikl} \frac{\partial^2 u_k}{\partial x_l \partial x_i} - \varepsilon_{ik} \frac{\partial^2 \varphi}{\partial x_k \partial x_i} = 0, \qquad (2)$$

where c_{ijkl} - mechanical stiffness tensor, e_{kij} - piezoelectric tensor, ε_{ik} is electric permittivity tensor, t is time.

In algorithm [1] the harmonic solutions of (1) - (2) equations are assumed with no attenuation. To calculate transverse SAW parameters, it is necessary to introduce non-zero imaginary attenuation coefficient γ which describes the wave attenuation along propagation direction x_i :

$$u_{j} = \beta_{j} \cdot \exp\left(-\alpha \frac{\omega x_{3}}{v}\right) \cdot \exp(i\omega t) \cdot \exp\left[-i\omega(1-i\gamma)\frac{x_{1}}{v}\right],$$

$$j = 1,2,3$$
(3)

$$\varphi = \beta_4 \cdot \exp\left(-\alpha \frac{\omega x_3}{v}\right) \cdot \exp(i\omega t) \cdot \exp\left[-i\omega(1-i\gamma)\frac{x_1}{v}\right], (4)$$

where β_{j} , β_{4} - displacement amplitudes of medium particles and electric potential, α - the wave attenuation along x_{3} direction (into the medium), ω - angular frequency, v - the SAW velocity. After putting (3) - (4) to (1) - (2) a homogeneous system of equations is achieved:

$$MAT*\beta^{T} = 0 \tag{5}$$

where: T - transposition, MAT - symmetrical matrix given by:

$$MAT = MAT 2 + MAT 1 + MAT 0$$
(6)

where:

$$\mathbf{MAT_2} = \begin{bmatrix} \mathbf{c}_{55} & \mathbf{c}_{45} & \mathbf{c}_{35} & \mathbf{e}_{35} \\ \mathbf{c}_{44} & \mathbf{c}_{34} & \mathbf{e}_{34} \\ \mathbf{c}_{33} & \mathbf{e}_{33} \\ \mathbf{c}_{33} & -\mathbf{\varepsilon}_{33} \end{bmatrix} \cdot \boldsymbol{\alpha}^2$$
(7)

$$\mathbf{MAT_1} = \begin{bmatrix} 2\mathbf{c}_{15} & (\mathbf{c}_{14} + \mathbf{c}_{56}) & (\mathbf{c}_{13} + \mathbf{c}_{55}) & (\mathbf{e}_{15} + \mathbf{e}_{31}) \\ 2\mathbf{c}_{46} & (\mathbf{c}_{36} + \mathbf{c}_{45}) & (\mathbf{e}_{14} + \mathbf{e}_{36}) \\ 2\mathbf{c}_{35} & (\mathbf{e}_{13} + \mathbf{e}_{35}) \\ & -2\mathbf{\epsilon}_{13} \end{bmatrix} \cdot \mathbf{i}\boldsymbol{\alpha} \cdot \mathbf{i}\boldsymbol{\gamma}$$
(8)

$$\begin{bmatrix} (-c_{11} + \rho v^2) & -c_{16} & -c_{15} & -e_{11} \\ (-c_{11} + \rho v^2) & -c_{16} & -e_{11} \end{bmatrix}$$
(9)

$$\mathbf{MAT_0} = \begin{bmatrix} (-c_{66} + \rho V) & -c_{56} & -e_{16} \\ (-c_{55} + \rho V^2) & e_{33} \\ & & \varepsilon_{11} \end{bmatrix} \cdot (i\gamma)^2$$

where c_{ij} *I*, J = 1, 2, ..., 6 and e_{ij} *i* = 1,2,3 are material tensors with abbreviated subscripts that are rotated in accordance with crystal orientation, ρ is crystal density. The evolving of (5) determinant yields 8th order polynomial with complex coefficients B_m , (m = 0, ..., 8), which are a function of velocity v, coefficient γ and material tensors:

$$B_8 \alpha^8 + B_7 \alpha^7 + B_6 \alpha^6 + B_5 \alpha^5 + B_4 \alpha^4 + B_3 \alpha^3 + B_2 \alpha^2 + B_1 \alpha^1 + B_0 = 0$$
(10)

Three roots with positive real parts are chosen from eight complex roots of polynomial (10). The roots must satisfy the condition of decaying amplitude along x_3 direction:

$$Re(\alpha^{(k)}) > 0 \quad k = 1, ..., 3$$
 (11)

One root must have negative real part:

$$Re(\alpha^{(4)}) < 0 \tag{12}$$

for mathematical modeling of partial leakage of acoustic energy inside the crystal.

The equation system (5) is solved for every $\alpha^{(k)}$, k = 1, ..., 4 root obtaining set of parameters $\beta_j^{(k)}$ (j, k = 1,...,4). One parameter β is set arbitrary non-zero value in each of the four solutions. A three order minor is chosen from matrix in equation (5). Putting $\alpha^{(k)}$ and $\beta_j(\mathbf{k})$ (j, k = 1,...,4) to wave equations (3) - (4) yields:

$$u_{j} = \sum_{k=1}^{4} A^{(k)} \beta_{j}^{(k)} \cdot \exp\left(-\alpha^{(k)} \frac{\omega x_{3}}{\nu}\right) \cdot \exp(i\omega t) \cdot$$
(13)

$$\cdot \exp\left[-i\omega(1-i\gamma) \frac{x_{1}}{\nu}\right],$$

$$\varphi = \sum_{k=1}^{4} A^{(k)} \beta_j^{(k)} \cdot \exp\left(-\alpha^{(k)} \frac{\omega x_3}{\nu}\right) \cdot \exp(i\omega t) \cdot \\ \cdot \exp\left[-i\omega(1-i\gamma) \frac{x_1}{\nu}\right],$$
(14)

where $A^{(k)}$ are parameters. Putting (13) - (14) to free surface boundary conditions yields homogeneous system of equations with variable $A^{(k)}$:

$$\sum_{k=1}^{4} \left[\beta_{1}^{(k)} \left[i \gamma c_{15} + \alpha^{(k)} c_{55} \right] + \beta_{2}^{(k)} \left[i \gamma c_{56} + \alpha^{(k)} c_{45} \right] + \beta_{3}^{(k)} \left[i \gamma c_{55} + \alpha^{(k)} c_{35} \right] + \beta_{4}^{(k)} \left[i \gamma e_{15} + \alpha^{(k)} e_{35} \right] \right] \cdot A^{(k)} = 0$$
(15)

$$\sum_{k=1}^{4} \left[\beta_{1}^{(k)} \left[i \gamma c_{14} + \alpha^{(k)} c_{45} \right] + \beta_{2}^{(k)} \left[i \gamma c_{46} + \alpha^{(k)} c_{44} \right] + \right.$$

$$\left. + \beta_{3}^{(k)} \left[i \gamma c_{45} + \alpha^{(k)} c_{34} \right] + \beta_{4}^{(k)} \left[i \gamma e_{14} + \alpha^{(k)} e_{34} \right] \right] \cdot A^{(k)} = 0$$

$$(16)$$

$$\sum_{k=1}^{4} \left[\beta_{1}^{(k)} \left[i \gamma c_{13} + \alpha^{(k)} c_{35} \right] + \beta_{2}^{(k)} \left[i \gamma c_{36} + \alpha^{(k)} c_{34} \right] + \beta_{3}^{(k)} \left[i \gamma c_{35} + \alpha^{(k)} c_{33} \right] + \beta_{4}^{(k)} \left[i \gamma e_{13} + \alpha^{(k)} e_{33} \right] \right] \cdot A^{(k)} = 0$$
(17)

$$\sum_{k=1}^{4} \left[\beta_{1}^{(k)} \left[i \gamma e_{31} + \alpha^{(k)} e_{35} \right] + \beta_{2}^{(k)} \left[i \gamma e_{36} + \alpha^{(k)} e_{34} \right] + \beta_{3}^{(k)} \left[i \gamma e_{35} + \alpha^{(k)} e_{33} \right] - \beta_{4}^{(k)} \left[i \gamma e_{13} + \alpha^{(k)} \varepsilon_{33} + \varepsilon_{0} \right] \right] \cdot A^{(k)} = 0$$
(18a)

For electrically shorted surface (metallized) instead of (18a) stands:

$$\sum_{k=1}^{4} \beta_4^{(k)} \cdot A^{(k)} = 0.$$
 (18b)

The determinant W of (15) - (18) equations system depends on material tensors and two variables: the velocity v and coefficient y. The velocity v and coefficient y are determined from two dimensional minimum of determinant W. The velocity v is a phase velocity.

The electromechanical coupling coefficient is given by the following dependence:

$$K^{2} = \frac{2 \left(v_{\rm f} - v_{\rm m} \right)}{v_{\rm f}},\tag{19}$$

where $v_{\rm f}$ and $v_{\rm m}$ are velocity under free and metallized surface, respectively.

The reflection coefficient of single electrode was calculated from dependence [2]:

$$r = 0.55 \cdot K^2$$
, (20)

which is true under conditions of infinitesimally thin metallization and strong electromechanical coupling in lithium tantalate. The wave attenuation coefficient in dimensions dB/ λ (where λ is a wavelength) is related to coefficient γ by the following:

$$\delta = 54.575 \cdot \gamma. \tag{21}$$

Acoustic power flow angle was calculated from a difference between phase and group velocity [2]:

$$\phi = \theta - \psi, \tag{22}$$

where θ is angle between X axis and phase velocity direction, while ψ was determined from slowness curve $1/v = f(\theta)$ under change of θ about $d\theta$, where $d\theta = 0.1^{\circ}$. There is a computer program implementing (1) - (22) formulas.

Theoretical AFP velocity and attenuation coefficient changes induced by interaction with Newtonian liquid are given by the dependencies derived from small perturbation analysis [7]:

$$\Delta \delta = k \cdot \frac{v v_2^2}{8\pi \cdot f \cdot P} \left(\sqrt{\eta' \cdot \rho'} + \sqrt{\eta \cdot \rho} \right), \qquad (23)$$

$$\Delta v = -\frac{v^2 v_2^2 \sqrt{\pi \cdot f}}{8\pi \cdot f \cdot P} \bigg(\sqrt{\eta' \cdot \rho'} - \sqrt{\eta \cdot \rho} \bigg), \qquad (24)$$

where: η and η' , ρ and ρ' - liquid viscosity and density before and after surface perturbation, respectively, v_2 - horizontal component displacement velocity, f - frequency, P - power flow angle module, k - wave vector module.

2.2. Calculation results

Parameters of SAW velocity under free and metallized surface, electromechanical coupling coefficient, attenuation coefficients under free and metallized surface, acoustic power flow angle and anisotropy coefficient $\partial \phi / \partial \theta$ were calculated from (1) - (22). Partial displacement amplitudes distributions along x₃ axis were calculated for free and metallized crystal surface. The calculations were made using four sets of material constants available in literature [3 - 6]. The results obtained for particular material constants sets are shown in Tab. 1.

Velocity under free and metallized surface oscillated from 4171 to 4226 m/s and from 4077 to 4112 m/s, respectively. Electromechanical coupling and reflection coefficients were from 4.54 to 5.56% and from 2.50 to 3.06%, respectively. Attenuation coefficients under free and metallized surface varied from 2.5 to 21 and from 11 to 79×10^{-5} dB/ λ , respectively. Attenuation coefficient turned out to be higher for free surface than for metallized surface only for materials constants [6]. Forward calculations and measurements are in good agreement with this result. Acoustic power flow angle was zero for all of the materials sets, while diffraction anisotropy coefficient $\partial \phi / \partial \theta$ varied from 2.44 to 2.74.

Amplitude displacement distributions under free and metallized surface are shown in Figs. 2a and b. Component u_2 – transverse horizontal is dominating. The electric conditions on the crystal surface determine the wave penetration distance. Under free surface the penetration distance becomes 15 times higher than under the metallized surface. The high penetration distance means that there is acoustic power leakage from surface into the crystal bulk. The surface metallization (electric short) induces energy concentration in the surface vicinity.

SAW velocity and attenuation coefficient changes versus liquid viscosity density product are shown in Fig. 3.



Fig. 2. Displacement amplitudes under free: – (a) and metallized (shorted) – (b) surface. **Rys. 2.** Amplitudy przemieszczeń cząstkowych przy powierzchni swobodnej – (a) i zwartej elektrycznie (metalizowanej) – (b).

Tab.	1.	Wyniki	obliczeń	parametrów	poprzecznej	AFP.
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36°YX LiTaO ₃	[3]	[4]	[5]	[6]
v _f [m/s]	4 171.7	4 211.3	4 226.3	4 214.5
<i>v</i> _m [m/s]	4 077.1	4 112.8	4 108.8	4 105.4
δ _f [dB/l]×10⁻⁵	3,9	2,5	21	17
$\delta_{\rm m}$ [dB/l]×10 ⁻⁵	16	79	26	11
K ² [%]	4.54	4.67	5,56	5.18
r [%]	2.50	2.57	3.06	2.85
<i>f</i> [°]	0.0	0.0	0.0	0.0
∂f/∂θ	2.44	2.61	2.74	2.68



Fig. 3. Theoretical changes of transverse SAW velocity $(\Delta v/v_0)$ and attenuation coefficient $(\Delta \delta)$ as a function of the root of viscosity and density product.

Rys. 3. Teoretyczne zmiany prędkości $(\Delta v/v_0)$ i współczynnika tłumienia fali poprzecznej AFP ($\Delta\delta$) w funkcji pierwiastka iloczynu lepkości i gęstości cieczy.

3. Measurements

3.1. Measurements of SAW parameters

A multimode synchronous rezonator was applied for transverse SAW measurements. The resonator (Fig. 4) data are: W = 1.5 mm, d = 2.99 mm, $p = 27.6 \mu$ m, $N_t = 5$ i $N_r = 200$, where W stands for aperture, d - distance between transducers, p - electrode period, N_t - electrode number of interdigital transducer and N_r - electrode number of reflector.

The resonator metallization was deposited on $36^{\circ}YX$ lithium tantalite, the aluminium thickness h_{AI} was about 0.1 µm. The measured amplitude response of the resonator is shown in Fig. 5. Shorted measurement circuit showed insertion loss about 1.2 dB. The amplitude response was measured using Agilent network analyzer 8753ET.

Two resonances are related to two vibration modes in the resonator. SAW parameters were determined from the comparison of the measured amplitude response with the calculated one. The velocity in periodically metallized interdigital area amounted to about 4136 ± 2 m/s, the velocity in continuously metallized area about 4101 ± 2 m/s, the electromechanical coupling coefficient about $2.35 \pm 0.1\%$. Determination of SAW velocity under free surface requires evaluation of the influence of metallization thickness. A resonator with metallization thickness h_{Al} about 0.2 µm was fabricated for this purpose. Determined SAW velocity under continuous metallization came to about 4106 ± 3 m/s and under periodical metallization to about 4140 ± 3 m/s. Below $h_{Al}/\lambda = 3,6 \cdot 10^{-3}$ ratio the velocity changes are linear with metallization thickness. Using (19) the determined velocity under free surface was noted to be about 4215 ± 15 m/s. High inaccuracy of the determination is due to the combination of SAW velocities and electromechanical coupling coefficient measurement inaccuracies. The measured SAW parameters are compared to the calculated ones in Tab. 2. The best measurement and calculation compatibility was obtained for material constants [6].



Fig. 4. Synchronous rezonator structure. **Rys. 4.** Struktura rezonatora synchronicznego.

Tab. 2. Comparison between measured and calculated SAW parameters in 36°YX LiTaO₃. **Tab. 2.** Porównanie obliczonych i zmierzonych parametrów AFP w 36°YX LiTaO₃.

36°YX LiTaO ₃	[5] 1990	[6] 1999	Measured in ITME 2013
v _f [m/s]	4 226.3	4 214.5	4215 ± 15
<i>v</i> _m [m/s]	4 108.8	4 105.4	4106 ± 3
K ² [%]	5.56	5.18	5.2 ± 0.1
r [%]	3.06	2.85	2.35 ± 0.1



Fig. 5. Amplitude response of the resonator as a function of frequency: a) measured, b) calculated. Rys. 5. Charakterystyki amplitudowe rezonatora w funkcji częstotliwości: a) zmierzone, b) obliczone.



Fig. 6. Double channel rezonator, top view (a), cross section (b). Rys. 6. Rezonator dwukanałowy, widok z góry (a), przekrój (b).

3.2. Measurements of viscosity and temperature

A water-glycerine solution was used to investigate transverse SAW interaction with liquid loading. In this case the viscosity is a known function of solution concentration and temperature. The measurements were carried out with the double channel resonator. The interdigital areas designed for the liquid loading were metallized in both channels (Fig. 6). The tunnel made of quartz was applied for shielding the transducer against liquid loading. Mounted with epoxy, the glue tunnel was about 2 mm high and about 0.5 mm thick.

Water glycerine solution was deposited using micropipette. After loading the interdigital area the insertion loss rose, while the resonance frequency was decreased (Fig. 7).



Fig. 7. The influence of liquid loading on to amplitude response in the frequency range of 74.2 - 75.2 MHz.

Rys. 7. Wpływ dociążenia cieczą na charakterystykę amplitudową rezonatora w zakresie częstotliwości 74,2 - 75,2 MHz.



Fig. 8. Insertion loss changes of resonator versus root of viscosity and density product.

Rys. 8. Zmiany tłumienności wtrąceniowej rezonatora w funkcji pierwiastka z iloczynu lepkości i gęstości.



Fig. 9. Changes of resonance frequency as a function of the root of viscosity and density product. **Rys. 9.** Zmiany częstotliwości rezonansowej w funkcji pierwiastka iloczynu lepkości i gęstości cieczy.

Loading	0	o n Concen- A	А.	f.	Λ Α .	∧f .		
30°C	[g/cm³]	[mPa·s]	√(ρ·η)	[%]	[dB]	[MHz]	[dB ¹]	[kHz]
water	1.00000	0.8	0.894427	0	-19.7	74.3559	0.0	0.00000
	1.0586	1.541	1.277225	24	-20	74.353	0.3	-39.00161
	1.09245	2.427	1.628305	37	-20.4	74.3485	0.7	-99.52136
Water-	1.1165	3.54	1.988067	46	-20.85	74.344	1.2	-160.04110
	1.13815	5.21	2.43511	54	-20.9	74.3425	1.2	-180.21435
glycerine	1.1601	8.26	3.095549	62	-20.98	74.341	1.3	-200.38760
	1.17935	13.27	3.956005	69	-21.22	74.3395	1.5	-220.56084
solution	1.1821	14.32	4.114325	70	-21.26	74.338	1.6	-240.73409
	1.19025	18.34	4.672171	73	-20.95	74.34	1.3	-213.83643
	1.19565	21.68	5.091335	75	-21.39	74.335	1.7	-281.08059
	1.20925	34.92	6.498231	80	-21.78	74.332	2.1	-321.42708
	1.20925	34.92	6.498231	80	-21.55	74.3365	1.9	-260.90734
	1.2279	77.5	9.755114	87	-22.4	74.329	2.7	-361.77358
	1.23585	115.3	11.93706	90	-23.2	74.323	3.5	-442.46657
Glycerine	1.26201	624	28.06233	100	-25.14	74.305	5.4	-684.54554

Tab. 3. The results of measurements of rezonator's parameters versus loading solution concentration. **Tab. 3.** Pomiary parametrów rezonatora w funkcji stężenia roztworu obciążającego.

The results of the mesurements of rezonator's parameters against solution concentration are given in Tab. 3. In Fig. 8 - 9 the changes of resonators parameters are showed as a function of root of viscosity and density product.

Temperature coefficient of frequency (TCF) was determined from measurements of resonance frequency changes in the temperature channel. For temperature stabilization a precision thermostat ITR-200 was applied and a constant phase method was used [9]. Relative frequency changes Df/f measured in 20.. 80°C range were linear with TCF = $-26 (\pm 1) \text{ ppm/°C}$.

4. Conclusions

Transverse horizontal displacements dominate in SAW in 36°YX LiTaO₃. SAW power leaks into the crystal bulk under free surface. Power concentration in the surface vicinity could be achieved by electrical short of the surface. The resonator operates properly when the interdigital area is metallized. Materials constants from [6] give calculations results in agreement with measurements results. Liquid loading of the interdigital area introduces systematic changes of the insertion loss and resonance frequency. Parameter changes are nonlinear and are not predicted by a small perturbation theory in most ranges of the investigated viscosities. The changes could be predicted only in the range from 0 to 2 kg·m⁻²·s^{-0.5} and in this range the rezonator can be a promising application for viscosity and temperature measurements.

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STRESZCZENIA WYBRANYCH PUBLIKACJI PRACOWNIKÓW ITME

Numerical design of Metal-Organic Vapour Phase Epitaxy process for gallium nitride epitaxial growth

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The paper presents the results of numerical simulations and experimental measurements of the epitaxial growth of gallium nitride in Metal Organic Vapor Phase Epitaxy within a AIX-200/4RF-S reactor. The aim was to develop optimal process conditions for obtaining the most homogeneous crystal layer. Since there are many factors influencing the chemical reactions on the crystal growth area such as: temperature, pressure, gas composition or reactor geometry, it is difficult to design an optimal process. In this study various process pressures and hydrogen volumetric flow rates have been considered. Due to the fact that it is not economically viable to test every combination of possible process conditions experimentally, detailed 3D modeling has been used to get an overview of the influence of process parameters. Numerical simulations increased the understanding of the epitaxial process by calculating the heat and mass transfer distribution during the growth of gallium nitride. Appropriate chemical reactions were included in the numerical model which allowed for the calculation of the growth rate of the substrate. The results obtained have been applied to optimize homogeneity of GaN film thickness and its growth rate.

High Q-Factor Millimeter-Wave Silicon Resonators

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Resonators made of high-resistivity silicon (HRS) have been manufactured, and their characteristics were measured at a frequency range from 20 to 50 GHz. To study the influence of the material resistivity on Q-factor values, two HRSs were used. The first one was as-grown high-purity floating zone (FZ) silicon with a resistivity of ~70 kQ \cdot cm. The second was FZ silicon irradiated with high-energy protons. The resistivity of the irradiated silicon was essentially the same as that of intrinsic silicon with a resistivity of ~400 kQ \cdot cm at room temperature. Several whispering gallery modes were identified and measured on disk shape samples made on both materials. At room temperature and at a frequency of 50 GHz, the Q-factor values for the resonators made of the asgrown and the irradiated silicon are up to 1.8×10^4 and up to 6×10^4 , respectively.

Ultrafast photocurrents at the surface of the three-dimensional topological insulator Bi₂Se₃

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Nature Communications, 2016, 7, 13259,

Three-dimensional topological insulators are fascinating materials with insulating bulk yet metallic surfaces that host highly mobile charge carriers with locked spin and momentum. Remarkably, surface currents with tunable direction and magnitude can be launched with tailored light beams. To better understand the underlying mechanisms, the current dynamics need to be resolved on the timescale of elementary scattering events (similar to 10 fs). Here, we excite and measure photocurrents in the model topological insulator Bi₂Se, with a time resolution of 20 fs by sampling the concomitantly emitted broadband terahertz (THz) electromagnetic field from 0.3 to 40 THz. Strikingly, the surface current response is dominated by an ultrafast charge transfer along the Se-Bi bonds. In contrast, photon-helicity-dependent photocurrents are found to be orders of magnitude smaller than expected from generation scenarios based on asymmetric depopulation of the Dirac cone. Our findings are of direct relevance for broadband optoelectronic devices based on topologicalinsulator surface currents.

Negative Kerr Nonlinearity of Graphene as seen via Chirped-Pulse-Pumped Self-Phase Modulation

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Physical Review Applied, 2016, 6, 4, 044006

We experimentally demonstrate a negative Kerr nonlinearity for quasiundoped graphene. Hereto, we introduce the method of chirped-pulse-pumped self-phase modulation and apply it to graphene-covered silicon waveguides at telecom wavelengths. The extracted Kerr-nonlinear index for graphene equals $n_{2,gr} = -10^{-13}$ m²/W. Whereas the sign of $n_{2,gr}$ turns out to be negative in contrast to what has been assumed so far, its magnitude is in correspondence with that observed in earlier experiments. Graphene's negative Kerr nonlinearity strongly impacts how graphene should be exploited for enhancing the nonlinear response of photonic (integrated) devices exhibiting a positive nonlinearity. It also opens up the possibility of using graphene to annihilate unwanted nonlinear effects in such devices, to develop unexplored approaches for establishing Kerr processes, and to extend the scope of the "periodic poling" method often used for second-order nonlinearities towards third-order Kerr processes. Because of the generic nature of the chirped-pulse-pumped self-phase modulation method, it will allow fully characterizing the Kerr nonlinearity of essentially any novel (2D) material.

Toxicity of different forms of graphene in a chicken embryo model

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Environmental Science and Pollution Research, 2016, 23, 19, 19940 – 19948

In the present work, the toxicity of three forms of graphene: pristine graphene (pG), graphene oxide (GO), and reduced graphene oxide (rGO) was investigated using a chicken embryo model. Fertilized chicken eggs were divided into the control group and groups administered with pG, GO, and rGO, in concentrations of 50, 500, and 5000 µg/ml. The experimental solutions were injected in ovo into the eggs, and at day 18 of incubation, the embryo survival, body and organ weights, the ultrastructure of liver samples, and the concentration of 8-hydroxy-2'-deoxyguanosine (8-OHdG) in the livers were measured. Survival of embryos decreased significantly after treatment with all types of graphene, but not in a dose-dependent manner. The body weights were only slightly affected by the highest doses of graphene, while the organ weights were not different among treatment groups. In all experimental groups, atypical hepatocyte ultrastructure and mitochondrial damage were observed. The concentration of the marker of DNA damage 8-OHdG in the liver significantly decreased after pG and rGO treatments. Further in vivo studies with different animal models are necessary to clarify the level of toxicity of different types of graphene and to estimate the concentrations appropriate to evaluate their biomedical applications and environmental hazard.

STEM study of Li₄Ti₅O₁₂ anode material modified with Ag nanoparticles

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Journal of Microscopy, 2016, 264, 1, 41 - 47

Comprehensive scanning transmission electron microscopy (STEM) analysis of Li₄Ti₅O₁₂ (LTO) powder modified by deposited Ag nanoparticles was performed. Nanocomposite powders with Ag content of 1 wt.%, 4 wt.%, 10 wt.% were fabricated in a chemical process from suspensions of Ag and LTO. Apart from the STEM results, the presence of pure silver on the surface of the ceramic powder was confirmed by XRD and XPS analyses. The silver particles deposited on the LTO particles were characterized using the EDS mapping technique. The quantified results of the EDS mapping showed a relatively homogenous distribution of silver nanoparticles on the powder surface for every metal content. The mean diameter of the nanoparticles deposited on the LTO powder was about 4 nm in all cases. An increase in the Ag content during chemical surface modification did not cause changes in the microstructure. Focusing on an analysis of the metallic nanoparticles on the ceramic powder, electron tomography was used as an investigative technique. A very precise analysis of three-dimensional nanostructures is desirable for a comprehensive analysis of complex materials. The quantified analysis of the Ag nanoparticles visualized using electron tomography confirmed the results of the size measurements taken from the two-dimensional EDS maps.

Roadmap on optical metamaterials

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Journal of Optics, 2016, 18,9, 093005, 53pp

Optical metamaterials have redefined how we understand light in notable ways: from strong response to optical magnetic fields, negative refraction, fast and slow light propagation in zero index and trapping structures, to flat, thin and perfect lenses. Many rules of thumb regarding optics, such as $\mu = 1$, now have an exception, and basic formulas, such as the Fresnel equations, have been expanded. The field of metamaterials has developed strongly over the past two decades. Leveraging structured materials systems to generate tailored response to a stimulus, it has grown to encompass research in optics, electromagnetics, acoustics and, increasingly, novel hybrid material responses. This roadmap is an effort to present emerging fronts in areas of optical metamaterials that could contribute and apply to other research communities. By anchoring each contribution in current work and prospectively discussing future potential and directions, the authors are translating the work of the

field in selected areas to a wider community and offering an incentive for outside researchers to engage our community where solid links do not already exist.

Stopping and straggling of H and He in ZnO

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The European Physical Journal D, 2016, 70, 9, 178

We present experimental and theoretical values for the energy loss of H and He ions in Zinc oxide, in mean value (stopping per unit path length) and mean square value (energy loss straggling). The measurements were carried out using the Rutherford Backscattering technique for (300-2000) keV H ions and (300-5000) keV He ions. Present experimental data are the first set of stopping and straggling values in this oxide. The theoretical research was encouraged considering the molecular description of ZnO as crystal solid using the density functional theory. The energy loss calculations for H and He ions with different charge states were performed with the shelwise local plasma approximation (SLPA). The molecular versus the Bragg-rule description is also discussed. The equilibrium charge state of He inside ZnO is analyzed based on the present stopping measurements, and a semiempirical charge state distribution is proposed. Present experimental and theoretical values show good agreement for both the stopping and the straggling. We also compare our data with the SRIM2013 and with CasP5.2 values.

Optical and X-Ray Topographic Studies of Dislocations, Growth-Sector Boundaries, and Stacking Faults in Synthetic Diamonds

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Crystals, 2016, 6, 7, 71

The characterization of growth features and defects in various high-pressure high-temperature (HPHT) synthetic diamonds has been achieved with optical and X-ray topographic techniques. For the X-ray studies, both characteristic and synchrotron radiation were used. The defects include dislocations, stacking faults, growth banding, growth sector boundaries, and metal inclusions. The directions of the Burgers vectors of many dislocations (edge, screw, and mixed 30 degrees, 60 degrees, and 73.2 degrees), and the fault vectors of stacking faults, were determined as < 110 > and 1/3 < 111 > respectively. Some dislocations were generated at metallic inclusions; and some dislocations split with the formation of stacking faults.

Aqueous biological graphene based formulations for ink-jet printing

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Polish Journal of Chemical Technology, 2016, 18, 2, 46 - 52

The aim of the study was to produce heterophasic graphene nanoplatelets based formulation designed for ink-jet printing and biomedical applications. The compositions should meet two conditions: should be cytocompatible and have the rheological properties that allow to apply it with ink-jet printing technique. In view of the above conditions, the selection of suspensions components, such as binder, solvent and surfactants was performed. In the first stage of the research the homogeneity of the dispersion of nanoplatelets and their sedimentation behaviour in diverse solutions were tested. Subsequently, the cytotoxicity of each ink on human mesenchymal stem cells was examined using the Alamar Blue Test. At the same time the rheology of the resulting suspensions was tested. As a result of these tests the best ink composition was elaborated: water, polyethylene glycol, graphene nanoplatelets and the surfactant from DuPont company.

Development of x-ray and ion diagnostics of plasma obtained with a 10-TW femtosecond laser

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Physica Scripta, 2016, 91, 7, 074008

Several x-ray and ion semiconductor detectors have been developed for the diagnostics of femtosecond laser plasma generated by a 10-TW laser which was recently commissioned for operation at the Institute of Plasma Physics and Laser Microfusion, Warsaw. A range of detectors has been employed including a CdTe detector for hard x-rays and four detectors for proton detection. These four are SiC and GaN employing a sandwich structure, an interdigitated M-S-M InP detector and finally a silicon photo-diode equipped with an aluminium filter (to shield against scattered light). The detectors presented are innovative as they are not commonly used for the diagnostic of laser plasma. The details of the internal structures of the detectors are presented. The immunity of the detectors to the noise coming from the laser system and the femtosecond plasma is discussed. Lastly, the possibility for further modifications and improvements are considered and discussed.

Characterisation of graphene-based layers for dye-sensitised solar cells application

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Surface Engineering, 2016, 32, 11, 816-822

The influence of the graphene-based counter electrode on the structure, optical properties and electrocatalytic activity of dye-sensitised solar cells (DSCC) was analysed. The graphene and reduced graphene oxide were deposited by CVD and spin-coating method on the FTO glass substrate, respectively. HRTEM investigation confirms the crystallographic structure of graphene. The investigated layers show flat transmittance spectra across the visible and near-infrared region. The charge transfer resistance of the graphene-based film was analysed by electrochemical impedance measurement. The obtained results show the possibility of replacing expensive platinum in DSCC by using graphene-based counter electrode.

InP nanowires quality control using SEM and Raman spectroscopy

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Materials Science-Poland, 2016, 34, 4, 851 - 855

Three different types of samples of InP nanowires, i.e. undoped, doped with Si and doped with Te, were grown and measured using SEM and Raman spectroscopy. Scanning Electron Microscope (SEM) images showed differences in the length, homogeneity and curvature of the nanowires. The most homogenous wires, grown most perpendicular to the surface, were those Si doped. They were also the shortest. Raman spectroscopy showed that the nanowires doped with Si had the lowest Full Width at Half Maximum (FWHM) TO band, which suggests the highest crystal quality of these wires. For the wires doped with Te, which were the most inhomogeneous, a low energy acoustic band was also observed, which suggests the lowest crystal quality of these structures.

Optical properties of transparent electrodes based on carbon nanotubes and graphene platelets

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Journal of Materials Science: Materials in Electronics, 2016, 27, 12, 12764 - 12771

Composite transparent electrodes based on carbon nanostructures such as multiwalled carbon nanotubes and graphene platelets were spray coated onto glass substrates and characterized by spectrophotometry and spectroscopic ellipsometry measurements. The dispersion relations of the ellipsometric angle rate, i.e. I<spacing diaeresis> and Delta versus wavelength lambda were measured in spectral range from 190 to 1700 nm. On the basis of these results, it was possible to estimate the value of the refractive index and extinction coefficient. Effective medium approximation model was chosen to calculate the optical constants of a mixed material. The average surface roughness and the average thickness of spray coated transparent resistive layers were also determined. The materials have a heterogeneous structure as confirmed by scanning electron microscopy and optical measurements (changes of depolarisation). From the Tauc plot it was possible to determine the energy gap. The influence of the coating process and the paint preparation on the optical properties was observed.

Impact of Different Conditions of Technological Process on Thermoelectric Properties of Fine-Grained PbTe

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¹ Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland Acta Physica Polonica A, 2016, 130, 5, 1255 - 1258

The aim of this work was to obtain PbTe material in the desired way in order to control the combined impact of lattice disorder, nanoscale precipitates and reduced grain sizes on the thermoelectric properties of this material. To achieve this, PbTe ingot doped with Ag was obtained by the Bridgman method, followed by ball-milling, cold pressing and sintering. In order to estimate crystallites diameters grain size measurements were carried out using the optical microscopy. Studies of electrical and thermoelectric properties of fine-grained material were performed. In order to analyze the morphology and the composition scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis also revealed presence of Ag-Te precipitates.

Effects of Carbon Allotropic Forms on Microstructure and Thermal Properties of Cu-C Composites Produced by SPS

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Journal of Materials Engineering and Performance, 2016, 25, 8, 3077 – 3083

Combination of extreme service conditions and complex thermomechanical loadings, e.g., in electronics or power industry, requires using advanced materials with unique properties. Dissipation of heat generated during the operation of high-power electronic elements is crucial from the point of view of their efficiency. Good cooling conditions can be guaranteed, for instance, with materials of very high thermal conductivity and low thermal expansion coefficient, and by designing the heat dissipation system in an accurate manner. Conventional materials such as silver, copper, or their alloys, often fail to meet such severe requirements. This paper discusses the results of investigations connected with Cu-C (multiwall carbon nanotubes (MWNTs), graphene nanopowder (GNP), or thermally reduced graphene oxide (RGO)) composites, produced using the spark plasma sintering technique. The obtained composites are characterized by uniform distribution of a carbon phase and high relative density. Compared with pure copper, developed materials are characterized by similar thermal conductivity and much lower values of thermal expansion coefficient. The most promising materials to use as heat dissipation elements seems to be copper-based composites reinforced by carbon nanotubes (CNTs) and GNP.

The Influence of Al₂O₃ Powder Morphology on the Properties of Cu-Al₂O₃ Composites Designed for Functionally Graded Materials (FGM)

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Journal of Materials Engineering and Performance, 2016, 25, 8, 3173 – 3184

In order to meet the requirements of an increased efficiency applying to modern devices and in more general terms science and technology, it is necessary to develop new materials. Combining various types of materials (such as metals and ceramics) and developing composite materials seem to be suitable solutions. One of the most interesting materials includes Cu-Al₂O₃ composite and gradient materials (FGMs). Due to their potential properties, copper-alumina composites could be used in aerospace industry as rocket thrusters and components in aircraft engines. The main challenge posed by copper matrix composites reinforced by aluminum oxide particles is obtaining the uniform structure with no residual porosity (existing within the area of the ceramic phase). In the present paper, Cu-Al₂O₃ composites (also in a gradient form) with 1, 3, and 5 vol.% of aluminum oxide were fabricated by the hot pressing and spark plasma sintering methods. Two forms of aluminum oxide (aAl2O3 powder and electrocorundum) were used as a reinforcement. Microstructural investigations revealed that near fully dense materials with low porosity and a clear interface between the metal matrix and ceramics were obtained in the case of the SPS method. In this paper, the properties (mechanical, thermal, and tribological) of composite materials were also collected and compared. Technological tests were preceded by finite element method analyses of thermal stresses generated in the gradient structure, and additionally, the role of porosity in the formation process of composite properties was modeled. Based on the said modeling, technological conditions for obtaining FGMs were proposed.

The Influence of the Particle Size on the Adhesion Between Ceramic Particles and Metal Matrix in MMC Composites

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Journal of Materials Engineering and Performance, 2016, 25, 8, 3139 – 3145

This study investigated the influence of the particle size on the adhesion force between ceramic particles and metal matrix in ceramic-reinforced metal matrix composites. The Cu-Al₂O₂ composites with 5 vol.% of ceramic phase were prepared by a powder metallurgy process. Alumina oxide powder as an electrocorundum (Al₂O₂) powder with different particle sizes, i.e., fine powder $< 3 \mu m$ and coarse powder of 180 µm was used as a reinforcement. Microstructural investigations included analyses using scanning electron microscopy with an integrated EDS microanalysis system and transmission microscopy. In order to measure the adhesion force (interface strength), we prepared the microwires made of the investigated materials and carried out the experiments with the use of the self-made tensile tester. We have observed that the interface strength is higher for the sample with coarse particles and is equal to $74 \pm A 4$ MPa and it is equal to $68 \pm$ A 3 MPa for the sample with fine ceramic particles.

Extending of flat normal dispersion profile in all-solid soft glass nonlinear photonic crystal fibres

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Journal of Optics, 2016, 8, 6, 065102

The bandwidth of coherent supercontinuum generated in optical fibres is strongly determined by the all-normal dispersion characteristic of the fibre. We investigate allnormal dispersion limitations in all-solid oxide-based soft glass photonic crystal fibres with various relative inclusion sizes and lattice constants. The influence of material dispersion on fibre dispersion characteristics for a selected pair of glasses is also examined. A relation between the material dispersion of the glasses and the fibre dispersion has been described. We determined the parameters which limit the maximum range of flattened all-normal dispersion profile achievable for the considered pair of heavy-metaloxide soft glasses.

Rheology of inks for various techniques of printed electronics

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Advanced Mechatronics Solutions, 2016, 393, 447 - 451

The inks and pastes with carbon nanoparticles, such as graphene nanoplatelets and carbon nanotubes, for diverse printed electronics techniques were produced. These composite materials, dedicated for screen printing, inkjet printing, spray coating and gravure printing were tested in context of their rheological properties. After comparing the obtained values of viscosity with standard values found in literature, it was confirmed that the tested suspensions may meet rheological requirements of particular techniques and can be transferred correctly on the substrate in the form of good quality pattern.

Assessment of Graphene Coatings Influence on Tribological Properties of Surfaces

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Advances in Intelligent Systems and Computing, 2016, 440, 781 - 788

This paper presents results of experiments carried out to determine influence of graphene coating on tribological

properties of surfaces of friction pairs. Within these experiments series of 24 h tribological tests of sliding friction between examined surfaces on specially designed measuring stand were conducted. Subject of study in these tests were electrolytic copper plated steel samples, additionally covered with graphene and, as a reference, identically prepared samples without the graphene layer. As a result of these experiments characteristics of coefficient of friction and temperature between surfaces, as well as changes in mass and roughness before and after tests were obtained. Based on these results improvement of tribological properties of sliding surfaces was shown.

Early stages of irradiation induced dislocations in urania

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Appl. Phys. Lett., 2016, 109, 181902

The early stages of nucleation and growth of dislocations by irradiation in urania is clarified based on the combination of experiments and atomistic calculations. It is established that irradiation induced dislocations follow a five stage process: (i) point defects are first created by irradiation, (ii) they aggregate into clusters, (iii) from which nucleate Frank loops, (iv) which transform into unfaulted loops via Shockley that in turn grow, and (v) finally reorganize into forest dislocations. Stages (i)-(iii) participate in the lattice expansion while the onset of lattice contraction starts with stage (iv), i.e., when unfaulted loops nucleate. Irradiation induced dislocations operate in the spontaneous recombination regime, to be opposed to the thermal diffusion regime. Body of arguments collaborates to this statement, the main one is the comparison between characteristic distances estimated from the dose rate (V-at/(K-0 x tau))(1/3) and from the diffusion coefficient (D x tau)(1/2). Such a comparison identifies materials under irradiation as belonging either into the recombination regime or not. Published by AIP Publishing.