Semiconductor surfaces structurization induced by ultrasound

R.K.Savkina

V.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine

Received November 28, 2011

Gallium arsenide and silicon substrates were exposed to cavitation impact induced by focusing a high-frequency acoustic wave into liquid nitrogen. Optical and atomic force microscopy methods as well as energy dispersive X-ray spectroscopy were used for analysis of the surface morphology and chemical composition of semiconductor surface. Microstructures formation as well as change of the chemical composition of the surface was found. The morphology of the structures is highly dependent on the acoustic parameters.

Образцы арсенида галлия и кремния подвергнуты воздействию кавитации, возбужденной в криогенной жидкости сфокусированным высокочастотным ультразвуком. Морфология поверхности обработанных образцов изучалась методом оптической и атомной силовой микроскопии, а также методом электронной микроскопии с элементным анализом. Обнаружено образование субмикронных структур и изменение химического состава поверхности. Морфология структур зависит от акустических параметров.

1. Introduction

Structurization and functionalization of semiconductor surfaces are important for many branches of science and technology [1]. Such surface properties as roughness, light reflectivity, chemical activity, and biocompatibility have a potential use in particular in electronics and medicine. For example, in standard technique for solar cells fabricating it is used silicon wafers with textured surfaces since surface texturing is well-established strategy for reducing reflection [2]. Surface structurization is also applied in MEMS [3]. Owing to development booster technologies such as reactive ion etching, isotropic etching, ashing/plasma cleaning manufacturing all silicon devices based on the scaling law became feasible [4]. Electrochemical etching of silicon has been utilized as a structurization technique to obtain micro-, meso- or macro-porous surfaces [5]. At the same time a wide range of topological features can be formed on the solid surfaces upon bombardment with ions [6, 7] as well as under irradiation with femto- and picosecond duration laser pulses [8].

Acoustic cavitation is a phenomenon observed when ultrasound of sufficient intensity is transmitted through a liquid causing micron-sized gas bubbles oscillation, growth, and violent explosion that results in extreme, but localized conditions within the collapsed cavities [9]. The bubble temperature reaches thousands of Kelvin degrees during collapse, pressure equals several hundreds of MPa, and heating and cooling rates are above 10^{10} K/sec. It should be also noted that plasma generation is possible in a cavitating liquid [10]. These extreme conditions are exploited for generating novel materials [11–13].

Application of cavitation phenomenon for solid surface structurization can be suggested as an attractive approach. However, untill recently it was difficult to control and to quantitatively reproduce cavitation. Controlled multibubble surface cavitation can be achieved by using a hydrophobic surface patterned with microcavities [14]. In addition, it is considered that megacycle ultrasound produces controlled acoustic cavitation and does not cause a damage of the surfaces.

In the previous work, suitable cavitation conditions to cause modification of gallium arsenide surface up to the microscale pattern formation as well as in a change in the chemical composition of semiconductor have been successfully revealed [15].

The current paper reports the results of the studyof complex structures formed on semiconductor substrate (Si and GaAs) under the exposure to the acoustic cavitation near liquid-solid interface. In the experiments ultrasonic cavitation was utilized to induce chemical and structural transformation of the semiconductor surface, creating features with a number of remarkable and potentially useful properties.

2. Experimental

The majority of the experimental work concerning acoustic cavitation has been performed in water and in several organic liquids at near the room temperature conditions. We have undertaken studies in cryogenic liquid such as nitrogen (LN_2). It should be noted that the operating temperature of LN_2 (78 K) is near the critical temperature of this fluid and thermodynamic effect of cavitation can be easily reached.

Two different types of materials, Si and GaAs, were treated in cryogenic liquid. Their main properties are described in Table. We used silicon 76.2 mm wafers and semi-insulating gallium arsenide 40 mm wafers. Samples were cut into 5 mm × 5 mm squares and were cleaned for 10 minutes in ethanol and then in distilled water. The initial surface roughness of the samples was found to be below 1 nm. The roughness is determined by the atomic force microscopy (AFM) method on a few randomly chosen areas of 2 × 2 μm.

Table. Material properties

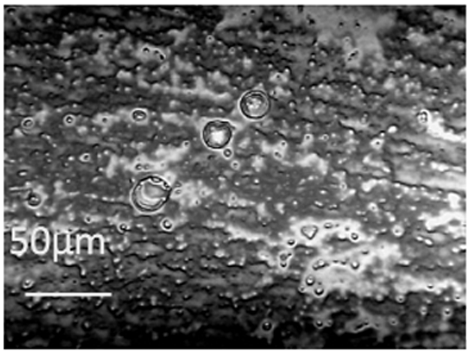
Parameters	Si	GaAs
Surface orientation	(100)	(001)
Density, $g \cdot cm^{-3}$	2.33	5.316
Enthalpy of fusion, $kJ \cdot mol^{-1}$	50.21	102.9
Melting point, K	1685	1238
Thermal conductivity (300 K), $W \cdot m^{-1} \cdot K^{-1}$	148	46
Specific heat, $J \cdot kg^{-1} \cdot K^{-1}$	710	330
Thermal diffusivity, $m^2 \cdot s^{-1}$	$9 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$
Volumetric thermal expansion coefficient, K^{-1}	$7 \cdot 10^{-6}$	$15 \cdot 10^{-6}$

The semiconductor surface was investigated by using optical microscopy (NV2E, Carl Zeiss Jena), atomic force microscopy (Digital Instruments NanoScope IIIa AFM operating in the tapping mode), and scanning electron microscopy (JSM-6490).

For cavitation activation, high frequency system (MHz) with focused energy resonator was used. It is known that the cavitation phenomenon occurs when acoustic intensity exceeds a certain threshold value. Utilization of the focusing in this experiment allowed increasing power of the high-frequency acoustic system as well as concentrating exposure on the exact position of the solid surface so as not to affect surrounding regions.

The experimental setup consisted of a reactor vessel and US equipment. Pumped stainless steel tank with internal copper cell filled with technical nitrogen was used for the reactor vessel. The experimental apparatus image is presented in [15]. Ceramic pie-

a)



b)

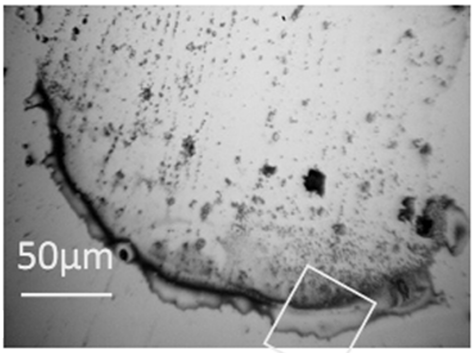


Fig. 1. Optical micrographs of GaAs sample exposed to the acoustic cavitation in liquid nitrogen at 3 MHz during 50 min (a) and at 6 MHz during 15 min (b).

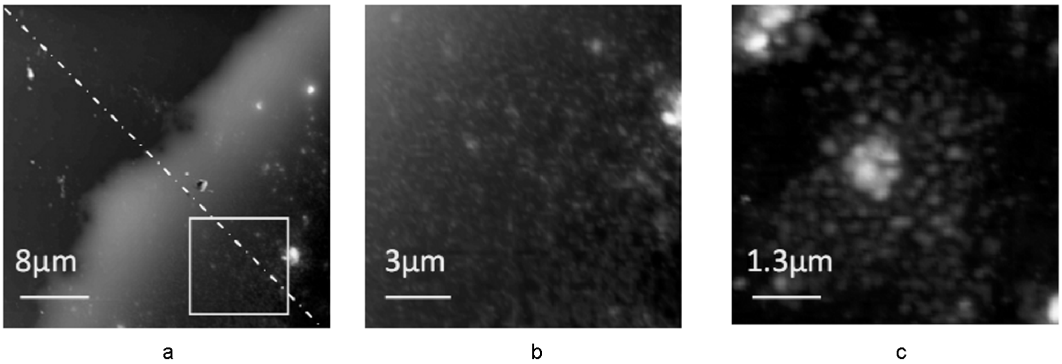


Fig. 2. AFM image of the GaAs surface exposed to the acoustic cavitation in liquid nitrogen at 6 MHz: (a) — framed on Fig. 1b, (b) — framed on Fig. 2a, (c) — cluster of nanostructures.

zoelectric transducer (PZT-19) with a diameter of 12 mm and resonant frequency of 3 MHz (or 6 MHz) acoustically drove the cell. The output voltage of US generator did not exceed 5 V, and the initial value of the acoustic intensity W_{US} did not exceed 1 W/cm^2.

Cylindrical copper concentrator (lens) was used for US intensity enhancement. Intensity gain of the acoustic system (PZT + copper lens) was about 58. The acoustic matching of the PZT to copper lens is sufficient for satisfying the condition of transparent boundary (~98 %). The acoustic impedance in liquid nitrogen (of the order of $0.7 \cdot 10^6$ $kgm^{-2}sec^{-1}$) is small as compared to the impedance of the copper lens (of the order of $3 \cdot 10^7$ $kgm^{-2}sec^{-1}$). As a consequence, the ratio of the emitted acoustic power to the dissipated power is about 55 %.

Semiconductor target was placed inside the acoustically driven copper cell in the focus region. The maximal value of pressure was about 8 bar in the focus of the acoustic system.

3. Results

3.1. *Gallium arsenide surface characterization using optical and atomic force microscopy*. The exposure of gallium arsenide substrate to megasonic cavitation in LN_2 leads to formation of micron-scale complex structures on the semiconductor surface. Fig. 1 shows the optical micrographs of the samples irradiated at varying acoustic parameters. After treatment of the GaAs sample at 3 MHz during 50 min in acoustically driven copper cell, a ripple-like pattern and small rounded bumps with micron size are formed (Fig. 1a). Small rings about 5–10 μm in diameter located in a random way are formed as well. The mean structure

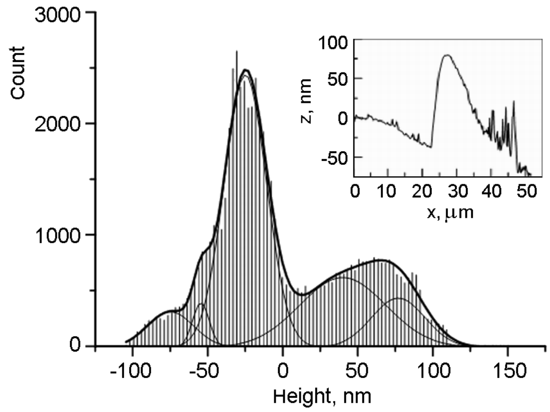


Fig. 3. The histograms of a distribution of submicron structures over its height. Inset: cross-sectional view of the surface along the diagonal in Fig. 2a.

height was estimated from the AFM data to be 300–500 nm as the modificated region integrally is below the original surface.

The reduction of acoustic intensity under the same frequency indices a reduction of effective size of the zone of liquid undergoing cavitation and thereby results in a decrease in the impact region. Character of the surface modification becomes more random with continuity violation. Small pits are also visible on the surface.

An increase of the processing frequency to 6 MHz results in the formation of separated circular regions with submicron structures inside (Fig. 1b). Fig. 2a–2c shows AFM image of the part of such region, and its profile is depicted in the inset of Fig. 3. AFM studies revealed the presence of a rim around the structured region. Interior of the circular region is below the original surface. Fig. 2b shows submicron structures inside circular region far from the rim. The roughness of the above-mentioned surface regions are described by surface height his-

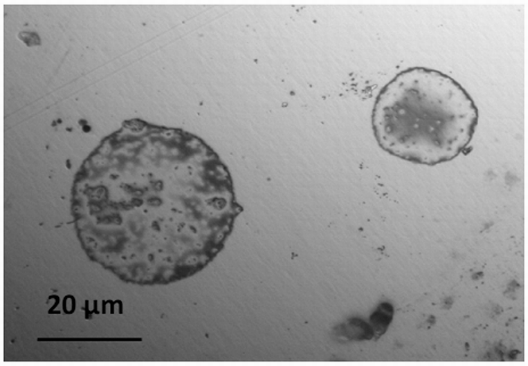


Fig. 4. Optical micrograph of Si sample exposured to the acoustic cavitation in liquid nitrogen at 6 MHz during 15 min.

tograms (see Fig. 3). In these histograms, several local maxima marked by arrows are seen. One can separate four groups of structures with typical heights h_i ~ 4.5 nm, 25 nm, 50 nm, and 75 nm. An average lateral size of structures has the order of 200–250 nm.

3.2. *Silicon surface characterization using optical microscopy and electron probe microanalysis*. As for gallium arsenide substrate the exposure of silicon to megasonic cavitation leads to the formation of micron-scale complex structures — separated circular regions with submicron structures inside and a rim around the structured region (Fig. 4). Fig. 5 presents electron micrograph of silicon surface which shows the creation of the dendritic micron-scale objects inside ultrasonically structured region. The chemical composition of the microstructured regions was investigated by means of energy dispersive X-ray spectroscopy (EDS). EDS analysis indicated the high oxygen concentration for structured areas as well as minor peaks corresponding to the following elements: P, S, K, Cl, and Ca were identified.

4. Discussion

It is necessary to note that the surface relief induced by the cavitation impact in Si and GaAs is similar in general: separated circular regions surrounded by the rim with submicron structures inside. Interior of the circular region is below the original surface. At the same time submicron structures inside circular regions are differed substantially for Si and GaAs samples. Moreover, Raman spectroscopy and energy dispersive X-ray spectroscopy data have confirmed the nitrogen atoms incorporation into GaAs lattice and Ga–N bond formation in the region of the maximal structural change due to the cavitation impact [15], whereas the nitrogen atoms incorporation into silicon lattice has not been revealed. In return, the dendritic micron-scale objects inside ultrasonically structured region were observed.

It is well known that ultrasound passing through a liquid causes thermal agitation, which in turn gives rise to the formation of superheated vapor bubbles [9, 16]. These bubbles are asymmetrically imploded with the ejection of micro-jets of solvent at speeds of up to several hundred m/s. On the basis of various theoretical studies and experimental data on cavitation-surface interaction, it is possible to assert that the micro-jet impact is a general physical mechanism responsible for the effect of cavitation on the solid surface. The potential energy of an expanded bubble is converted into the kinetic energy of a liquid jet which transfers energy to the substrate atoms at the site of impact. Here, surface patterns are generated by "initial" bubbles, formed in the liquid, and by "secondary" bubbles, which are formed at the site of initial jet impacts.

Since we deal with multibubble cavitation in an acoustic field, the bubbles can

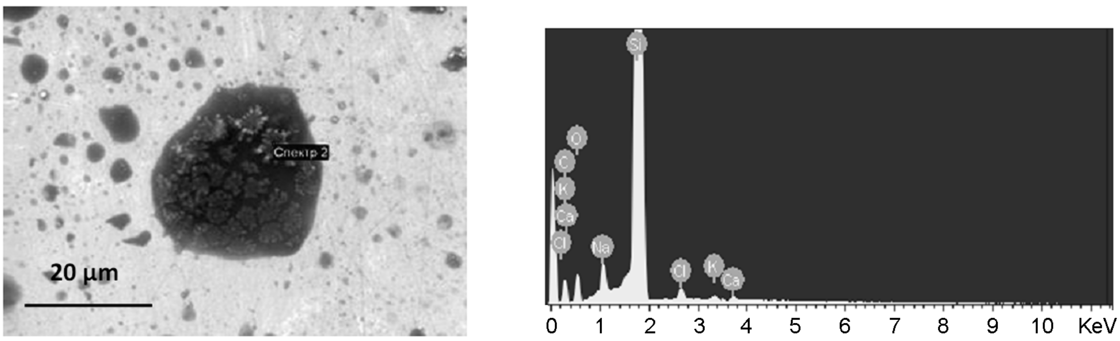


Fig. 5. Electron micrograph and the atomic composition of the microstructured silicon surface exposured to the acoustic cavitation in liquid nitrogen at 6 MHz during 15 min.

interact among themselves with formation of compact groups, which considered as small or large clusters. A distinguishing characteristic of the large clusters is that they can be attracted by the surface and frequently look like attached hemispheres under the influence of surface tension [17].

Apparently, the surface relief depicted in Fig. 1a is generated as a result of micro-jet impacts during collapses of both "initial" and "secondary" bubbles. At the same time, circular regions shown in Fig. 1b and Fig. 4 demonstrate the collective bubbles behavior. According to traces on the surface, we deal with large clusters with maximum radius up to the millimeter range.

The character of the surface structurization induced by cavitation impact is decisively determined by the binding energy and the crystal structure of the base solid. It is known that micro-jets may cause the shattering of hard brittle solids and this is exploited, for example, within medicine for the shattering of kidney stones. Soft solid surfaces such as polymers surfaces, however, are ablated by such jets [16].

GaAs is very susceptible to mechanical damage. In the case of GaAs the transition from brittle to ductile state is estimated to be above 400°C, below this temperature the material is extremely brittle [18]. Brittle materials are deformed by cracking under collapsing bubbles exposure. However, we have not observed cracking under GaAs treatment. For silicon transition from brittle to ductile state can be observed at around 500°C. But, in our experiments we have not observed cracking under Si surface treatment too.

It can be suggested that a high density of energy transferred to the substrate atoms from the jet impact results in a local melting of a shallow layer of the semiconductor around the impact spot. The formation of the rim around circular regions confirms this assumption. Because of the difference in densities of the hot fluidized material and the surrounding crystalline material and also due to local tensions and elastic rebound of the bulk, the liquid melt is pushed away from the surface. The subsequent rapid quenching of the melted material results in the formation of structures inside circular regions which is surrounded by the rim. Due to significant material intermixing in the collision spot there is a probability for some of the nitrogen atoms to get stuck in the semiconductor target during its re-solidification that was observed for GaAs.

In terms of radiation damage and energy transfer from micro-jet to the material, it would be expected that at identical treatment conditions nitrogen micro-jet should produce less locally melted volume at the point of collision in Si than in GaAs because silicon has a higher melting temperature than GaAs. Thermal conductivity and thermal diffusivity of GaAs is much lower compared to Si (see Table). It means that it takes longer for the melt of GaAs to cool down.

It is also necessary to mentioned that dendrite formation inside ultrasonically structured region of Si can points to the melted silicon supercooling as a result of the solidification point shift due to high pressure pulses associated with a collapsing bubble.

4. Conclusions

Thus, array of microstructures was successfully formed on the surfaces of gallium arsenide and silicon using processing them in cavitating cryogenic liquid. The creation of the dendritic objects inside ultrasonically structured region of the silicon substrate was observed.

It was found that the morphology of the structures is highly dependent on the acoustic parameters. Decrease of the characteristic dimensions of structures on the semiconductor surface from micron to submicron at a frequency variation from 3 MHz to 6 MHz occurs and can be explained by the decrease of the mean (?) bubbles size. In addition, the character of the surface structurization induced by cavitation impact is determined by the type of the semiconductor target.

Acknowledgment. The author is grateful to Dr.O.Litvin and Dr.V.Tinkov for their helpful cooperation with the surface characterizations as well as to Dr.A.Smirnov for comments and fruitfull discussions.

References

1. A.Gorecka-Drzazga, *Opt. Appl.*, **37**, 341 (2007).
2. A.Green Martin, Solarcells: Operating Principles, Technology and System Applications, University of New South Wales, Kensington (1992).
3. M.Gad-el-Hak, The MEMS Handbook, CRC Press LLC (2002).
4. H.Abe, M.Yoneda, N.Fujiwara, *Japanese J. Appl. Phys.*, **47**, 1435 (2008).
5. H.Foll, M.Christophersen, J.Carstensen et al., *Mater. Sci. and Engin. R: Reports*, **39**, 93 (2002).

6. L.S.Dake, D.E.King, J.R.Pitts, A.W.Czanderna, Beam Effects, Surface Topography, and Depth Profiling in Surface Analysis, ed. by A.W.Czanderna, T.E.Madey and C.J.Powell, Plenum Press, New York (1998).
7. J.B.Malherbe, Bombardment-induced Topography on Semiconductor Surfaces, in: Ion Beam Analysis of Surfaces and Interfaces of Condensed Matter Systems, ed. by P.Chakraborty, Nova Science Publ., New York (2003), p.357.
8. S.R.Foltyn, Pulsed Laser Deposition of Thin Films, ed. by D.B.Chrisey and G.K.Hubler, Wiley-Interscience, New York (1994).
9. K.S.Suslick, D.J.Flannigan, *Annu. Rev. Phys. Chem.*, **59**, 659 (2008).
10. D.J.Flannigan, K.S.Suslick, *Phys. Rev. Lett.*, **95**, 044301 (2005).
11. K.S.Suslick, M.M.Fang, T.Hyeon, M.M.Mdleleni, Applications of Sonochemistry to Materials Synthesis, in: Sonochemistry and Sonoluminescence, ed. by A.Crum, Kluwer Publishers, Dordrecht, Netherlands (1999), p.291.
12. A.Gedanken, *Ultrason. Sonochem.*, **11**, 47 (2004).
13. A.Gedanken, Ultrasonic Processing to Produce Nanoparticles, in: Encyclopedia of Materials: Science and Technology, ed. by K.H.J.Buschow, R.W.Cahn, M.C.Flemings et al., Elsevier Science, Oxford (2001), vol.10, p.9450-6.
14. N.Bremond, M.Arora, C.D.Ohl, D.Lohse, *Phys. Rev. Lett.*, **96**, 224501 (2006).
15. R.K.Savkina, A.B.Smirnov, *J. Phys. D:Appl. Phys.*, **43**, 425301 (2010).
16. K.S.Suslick, *Science*, **247**, 1439 (1990).
17. R.Mettin, Bubble Structures in Acoustic Cavitation, in: Bubble and Particle Dynamics in Acoustic Fields: Modern Trends and Applications Research Signpost, ed. by ed A.A.Doinikov, Kerala, India (2005), p.1.
18. P.Paufler, G.Wagner, K.Grosse, *Cryst. Res. and Techn.*, **28**, 3 (1993).

Структуризація напівпровідникових поверхонь, індукована ультразвуком

Р.К.Савкіна

Зразки арсеніду галію і кремнію піддано впливу кавітації, збудженої у кріогенній рідині сфокусованим високочастотним ультразвуком. Морфологія поверхні оброблених зразків вивчалася методом оптичної та атомної силової мікроскопії, а також методом електронної мікроскопії з елементним аналізом. Виявлено утворення субмікронних структур і зміну хімічного складу поверхні. Морфологія структур залежить від акустичних параметрів.