Mater. Res. Soc. Symp. Proc. Vol. 1534 © 2013 Materials Research Society
DOI: 10.1557/opl.2013.304

Nanoscale Structuration of Semiconductor Surface Induced by Cavitation Impact

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ABSTRACT

The results of studies of the complex structures formed on the semiconductor substrates exposed to the acoustic cavitation (AC) near the liquid-solid interface are reported. Gallium arsenide and silicon substrates were exposed to the cavitation impact initiated by the focusing a high-frequency (MHz) acoustic wave into the liquid nitrogen. Optical, atomic force and scanning electron microscopy methods as well as energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy were used for analysis of the surface morphology and chemical composition of semiconductor compounds. The formation of separated circular regions with the nanostructured surfaces inside was found. Electron micrograph images of the silicon surface show the creation of the dendritic objects inside of the ultrasonically structured region. The Raman spectroscopy and EDS data have confirmed the change of the chemical composition of the structured gallium arsenide surface and the Ga-N bond formation. The incorporation of nitrogen atoms into a silicon lattice has not been observed while XRD results have shown the formation of silicates of alkali metals on the silicon surface.

INTRODUCTION

Interactions of the energetic flows beams with the solid surfaces demonstrate unique phenomena and promise new applications for surface modification technology. Solid surfaces can develop a wide range of useful topological features upon bombardment with ions, clusters of atoms and molecules, as well as on laser processing as a result of the deposition of large amounts of energy in the form of heat and pressure or as a result of the plasma effect.

It is well known that ultrasonic cavitation also creates extreme energetic conditions with the local temperatures of about 5000K and the pressure of several hundred MPa [1]. It is necessary to notice also the possibility of the plasma generation in a cavitating liquid [2]. These extreme conditions are widely used in chemistry, as for example to synthesize nanoparticles [3], to enhance the electrochemical reactions and to modify the surface properties of electrodes [4], as well as to generate the novel materials in a liquid medium [5-7], etc.

Cavitation near extended liquid-solid interfaces is very different from cavitation in pure liquids. The impingement of microjets and shockwaves on the surface creates the localized erosion, which can generate newly exposed, highly heated surface and even eject matter from the surface. This is a grave disadvantage in many industrial systems. Despite corrosion problem, the controlled cavitation near a solid surface proves a powerful tool for modern technologies like the salmonella destruction [8], the treatment of kidney stones [9], producing the hydrogenated/ deuterated metallic powders by sonoimplantation [10], etc.

With respect to semiconductors, the main application of acoustic cavitation is the ultrasonic cleaning. At the same time, we think that the combination of the factors, which accompany bubbles collapse near the semiconductor surface, can results in semiconductor surface structuration up to a synthesis of a new phase. Possibility of the application of acoustic cavitation for the material deposition from a solution on the semiconductor surface was confirmed by the results obtained in [11].

Earlier we presented experimental results on the modification that occurs on the gallium arsenide surface subjected to the megasonic cavitation exposure [12]. The nitrogen atoms incorporation into the GaAs lattice and the Ga-N bond formation in the region of the maximal structural change due to the cavitation impact was found.

In the present paper, we report the effects of megasonic cavitation on the several semiconductor surfaces. Silicon and gallium arsenide samples were studied. Experiments employ the cavitation in an attempt to drive the chemical and structural transformations on a semiconductor surface, creating features with a number of remarkable and potentially useful properties.

EXPERIMENTAL DETAILS

We have undertaken studies of the cavitation impact in cryogenic liquid such as nitrogen (LN_2). The experimental setup consisted of a reactor vessel and the ultrasonic (US) equipment. A pumped, cylindrical stainless steel tank with the internal copper cell filled with technical nitrogen was used for the reactor vessel [12]. A ceramic US transducer (PZT-19) operating at 3 MHz (or 6 MHz) with a diameter of 12 mm was installed in the copper cell.

It is well known that at high sonic frequencies, on the order of the MHz, the production of cavitation bubbles becomes more difficult than at low sonic frequencies, of the order of the kHz. To achieve cavitation, the intensity of the applied sound must be increased. In our experiments, for the cavitation activation, a high frequency system (MHz) with focused energy resonator was used. Besides, the operating temperature of LN_2 (78 K) is near the critical temperature of this fluid, and the thermodynamic effect of cavitation can be easily reached.

The initial value of an acoustic intensity W_{US} did not exceed 1 W/cm^2. A cylindrical copper concentrator (lens) was used and the intensity gain of the acoustic system (PZT + copper lens) was about 58. The acoustic matching the PZT to copper lens is sufficient for satisfying the condition of transparent boundary (~98%). The impedance mismatch at the interface between the concentrator and LN_2 has led to the fact that the ratio of the emitted acoustic power to the dissipated power was about 55%. And the maximal value of pressure in the focus of the acoustic system was about 8 bars.

Two different types of materials, Si (001) and GaAs (001), were treated in a cryogenic liquid. We have used silicon wafers with diameter about 76.2-mm and semi-insulating gallium arsenide wafers with diameter about 40 mm. The samples were cut into the 5 mm× 5 mm squares and were cleaned for 10 minutes in ethanol and then in distilled water. The initial surface roughness of samples was found below 1nm.

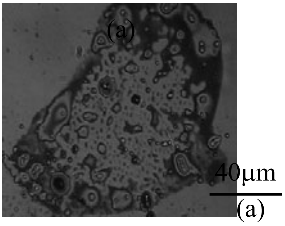
A semiconductor sample was placed inside of the acoustically driven copper cell in the focus region. After sonication the semiconductor surface was investigated using the optical microscopy (NV2E, Carl Zeiss Jena), atomic force microscopy (AFM) (Digital Instruments NanoScope IIIa AFM operating in the tapping mode), and scanning electron microscopy (SEM) (JSM-6490). The energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy were used as well.

RESULTS AND DISCUSSION

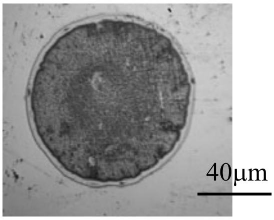
The exposure of semiconductor wafers to megasonic cavitation in LN_2 leads to the surface structuration. After a treatment of GaAs sample at 3 MHz in an acoustically driven copper cell, ripple-like patterns are developed [13]. Micron size rounded bumps and rings about 5-10 μm in diameter located in a random way are formed as well (see figure 1a). The modified region integrally is below of the original surface. A treatment of the Si sample at the same conditions leaded to the similar results.

It was revealed that the characteristic dimension of the structures on the semiconductor surface depends on the exposure parameters and can be controlled by the regulation of an acoustic frequency. The reduction of acoustic intensity at the same frequency results to a more random character of surface modifications.

The increase in a processing frequency changes both the species and the size of the structures formed on the surface. The formation of separated circular regions with nanostructured insides is observed (see figure 1b).



(a)



(b)

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

AFM studies revealed the presence of a rim around the structured region. The interior of circular region is located below of the original surface. Figures2a, 2b, and 2c show the AFM images of such region. The roughness of the above-mentioned surface regions are described by the surface height histograms (see figures 2d, 2e, and 2f). In these histograms, several local maxima are seen. One can separate the several groups of structures with the typical heights of h_i ~3-8 nm and~11-15 nm for GaAs as well as ~30 nm and ~ 70 nm for Si substrates.

Thus, it should be noted the similarity of the relief produced on GaAs and Si surfaces at the cavitation.

At the same time, there were found the distinctive features for each semiconductor studied. It was found that the prolonged cavitation treatment of silicon wafer resulted in the dendritic structure formation. Figure 3 presents the optical (Inset) and SEM images of the silicon surface that show the creation of dendritic objects inside of the ultrasonically structured region and a content of different atoms incorporated into the structured silicon surface exposed to the acoustic cavitation.

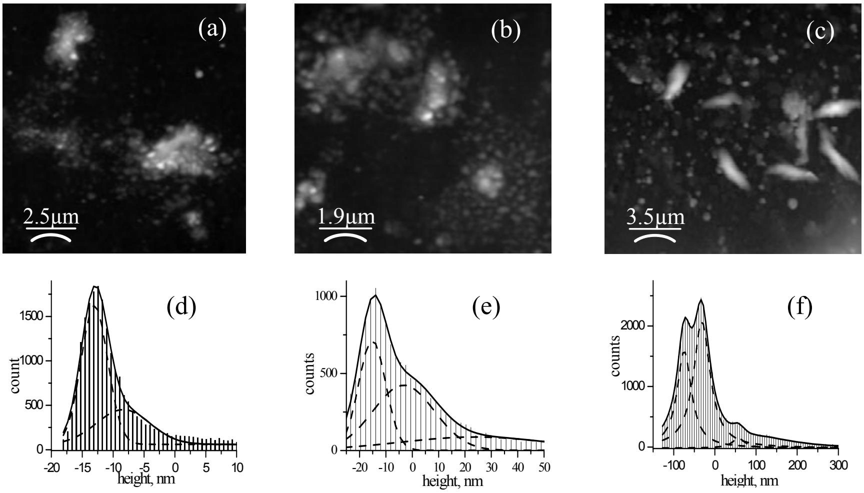


Figure 2.AFM images of the GaAs (a, b) and Si (c) surfaces exposed to the acoustic cavitation in the liquid nitrogen at 6MHz; (d), (e), (f) - corresponding histograms of a height distribution over the structures.

Chemical properties of nanostructured semiconductor surface

It was found that various gaseous atoms (including nitrogen) can be strongly implanted into the metal powders under ultrasonic cavitation [10]. In our experiment, one can expect that significant material intermixing in the impact sites takes place, and there is a probability for nitrogen atoms to be incorporated into a semiconductor wafer in the modificated region.

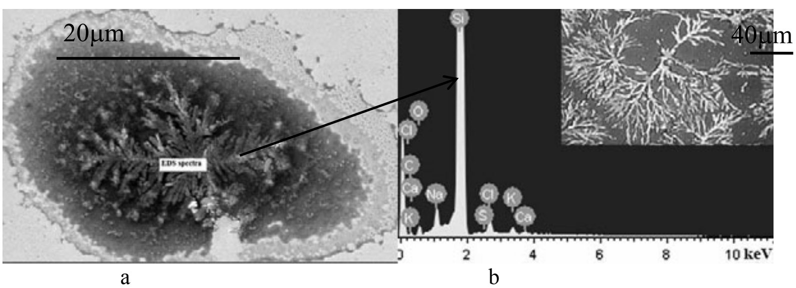


Figure 3. SEM micrograph (a) and the atomic composition of the structured silicon surface (b) exposed to the acoustic cavitation in liquid nitrogen at 6 MHz during 15 min. Inset: an optical image of silicon surface exposed to the acoustic cavitation during 1 hour.

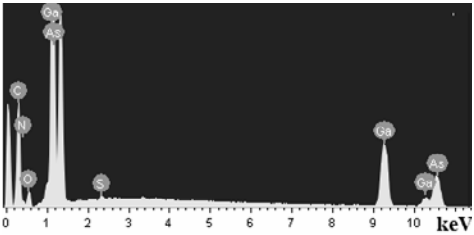


Figure 4. The atomic composition of structured gallium arsenide surface exposed to the acoustic cavitation in liquid nitrogen at 3 MHz.

The atomic composition of microstructured gallium arsenide surfaces was investigated using EDS. The chemical composition of samples was studied in numerous randomly selected areas of 5 × 5 μm. We found an inhomogeneous character of the nitrogen atom incorporation into the substrate lattice (from 5% to 7.5%) after the cavitation exposure. EDS analysis also indicated the presence of oxygen and carbon atoms in the nitrated areas (see figure 4).

Moreover, the Raman spectroscopy data has confirmed the nitrogen atom incorporation into the GaAs lattice and the Ga-N bond formation in the region of the maximal structural change at the cavitation impact [12]. At the same time, the nitrogen atom incorporation into the silicon lattice has not been observed while we identified the peaks corresponding to the following elements: Na, S, K, Cl, and Ca (see figure 3b). Figure 5 represents the XRD result for the Si(100) substrate before and after the cavitation treatment.

The XRD pattern for an initial state reveals only the Si 400 diffraction peak that indicates (001) orientation of the substrate.

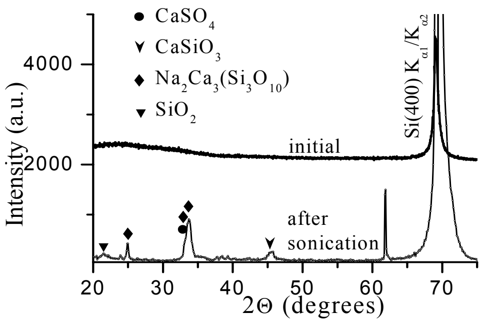


Figure 5.XRD patterns of silicon substrate before and after exposure to cavitation impacts. The crystallographic database WWW-MINCRYST [14] was used for peaks identification.

The presence of higher intensity background in the range of 2θ= 20-30 degrees in XRD pattern for the initial state denotes the existence of a small amount of amorphous phase on the Si substrate surface, obviously the amorphous Si oxides. A new peaks connected with the formation of some compounds are observed in XRD pattern obtained after the cavitation treatment. In particular, we found the formation of silicates and sulfates of alkali metals. The broad diffraction peak appeared at $2\theta = 21.5^{o}$ shows the formation of SiO_2 nanocrystals at the cavitation treatment.

CONCLUSIONS

Gallium arsenide and silicon substrates exposed to the cavitation impact, obtained by focusing a high frequency acoustic wave into liquid nitrogen, were investigated. Based on the experimental results, the following conclusions can be drawn.

The exposure of semiconductor substrate to megasonic cavitation in LN_2 leads to the surface structuration. It was revealed that the characteristic dimension of the peculiarities on the semiconductor surface depended on the exposure parameters and can be controlled (from micron- to nano-scale dimension) by the regulation of an acoustic frequency. The change of the chemical composition of the semiconductor surface was also found. EDS analysis indicated on the nitrogen atom incorporation into the gallium arsenide lattice. XRD results showed the formation of silicates of alkali metals on the silicon surface as well.

REFERENCES

1. K. S. Suslickand D. J. Flannigan, *Annu. Rev. Phys. Chem.* **59**, 659 (2008).
2. D. J. Flannigan and K.S. Suslick*, Phys. Rev. Lett.* **95**,044301 (2005).
3. Y. Mastai and A. Gedanken,"Sonochemistry and other novel methods developed for synthesis of nanoparticles", *The Chemistry of Nanomaterials: Synthesis, Properties and Applications,*edited by C. N. R. Rao, A. Müller, and A. K. Cheetham (WILEY-VCH, 2004) pp.113-207.
4. T. J. Mason, J. P. Lorimer and D. J. Walton, *Ultrasonics* **28**, 333 (1990).
5. M. Ashokkumar and T. Mason,*SonochemistryinKirk-Othmer Encyclopedia of Chemical Technology* (John Wiley and Sons, 2007).
6. A. Gedanken, *Ultrasonics Sonochemistry* **11**, 47 (2004).
7. N. Perkas, Y. Wang, Y. Koltypin, A. Gedanken, and S. Chandrasekaran, *Chem. Comm.* **11**, 988 (2001).
8. D. M. Wrigley and N. G. Llorca, *Journal of Food Protection* **55**, 678 (1992).
9. Y. A. Pishchalnikov, O. A. Sapozhnikov, M. R. Bailey, J. C. Williams Jr, R. O. Cleveland, T. Colonius, L. A. Crum, A. P. Evan, and J. A. McAteer, *J.Endourol.* **17**, 435 (2003).
10. Y. Arata and Y.-C. Zhang, *Appl. Phys. Letters* **80**, 2416 (2002).
11. S. Nomura and H. Toyota, *Appl. Phys. Letters* **83**, 4503 (2003).
12. R. K. Savkina, A. B.Smirnov, *J. Phys. D: Appl. Phys.* **43**, 425301 (2010).
13. R. K. Savkina, *Functional material,* **19**, 38(2012).
14. http://database.iem.ac.ru/mincryst.