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Patterning of Photoluminescent Nanostructured Spots on Silicon by Air Optical Breakdown Processing

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Nanostructured silicon can exhibit visible photoluminescence (PL) with quantum efficiency of up to few percent, although bulk silicon has a small (1.11 eV) and indirect band gap. This luminescent property gives a promise fo the creation of Si-based optoelectronics devices and their potential integration in standard Si-based microelectronics chips. The search of methods for the production of visible light-emission from Si-based materials becomes currently a great task and a subject of numerous studies, while "dry" fabrication techniques are of particular interest due to a much better compatibility with silicon processing technology.

We have recently demonstrated a novel "dry", vacuum-free laser-assisted method for a fabrication of nanostructured Si/SiO_x layers on a silicon wafer[1]. This method uses the phenomenon of air optical breakdown to modify the semiconductor surface. The radiation of a pulsed TEA CO_2 laser (10.6 μm, pulse energy 1 J, pulse length 1 μs FWHM, repetition rate 3 Hz) was focused by a Fresnel's lens on different silicon wafers (N- and P-type, resistance 0.01- 10 Ohm·cm) to initiate the optical breakdown in atmospheric pressure air. After several breakdown initiations near the threshold of plasma production, a gray-tint layer was formed under the radiation spot on the silicon surface. The size of the processed area could be varied from hundreds of microns to millimeters b varying the radiation focusing conditions.

As shown in Fig. 1, the silicon surface treated by 10 laser shots contained nanoscale holes, between 30 and 150 nm in diameter. However, smaller holes, not resolved by SEM, may still be additionally present. A prolonged treatment of the silicon surface led to a formation of columns and channels with similar dimensions. For samples treated under the threshold of plasma initiation, SEM studies did not detect the presence of the ablated material outside the treated area on the free target surface.

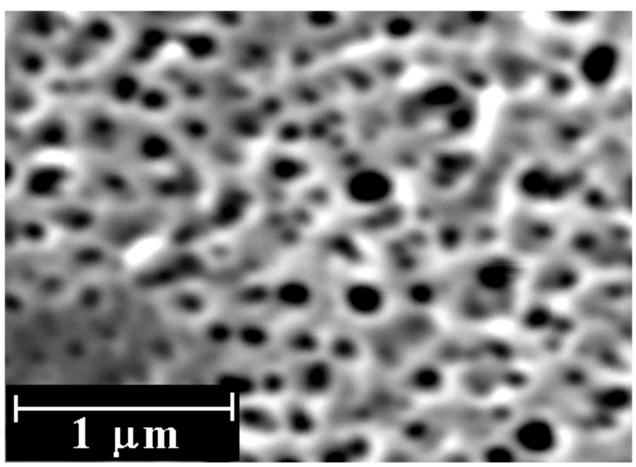

Fig. 1. Typical SEM image of a silicon target surface under the radiation spot after 10 breakdown initiations near the plasma ignition threshold.

X-ray photoelectron spectroscopy (XPS) spectra of all samples demonstrated a single peak at about 104 eV. This peak is always assigned to 2p photoelectrons of pure SiO_2, suggesting that the processed layer mainly consisted of silicon dioxide. Nevertheless, X-ray Diffraction (XRD) spectra contained peaks associated with different crystallin silicon phases, suggesting that silicon crystals are present in the layers. This gives the evidence that the resulting layers consisted of silicon crystals embedded in SiO_2 matrix. A rough estimation of the minimal crystal size from a broadness of typical crystalline silicon peaks by the Debye-Scherrer formula gave the value about 10 nm. The porosity of layers estimated from of Specular X-ray Reflectivity (SXRR) spectra was about 75-80%.

The processed area exhibited strong PL signals, which could be easily seen by naked eyes. Fig. 2 shows that a typical PL spectrum from the breakdown-treated area had a main emission band in red range around 1.9-2.0 eV. The peak position was independent of the extent of the surface treatment, type of silicon wafer (N- or P-) and doping level. The PL signals were relatively stable to a prolonged illumination of the layers by the radiation of an Ar^+ laser. In particular, the decrease of their integral intensity did not exceed 40% even after 6 hours of the continuous illumination.

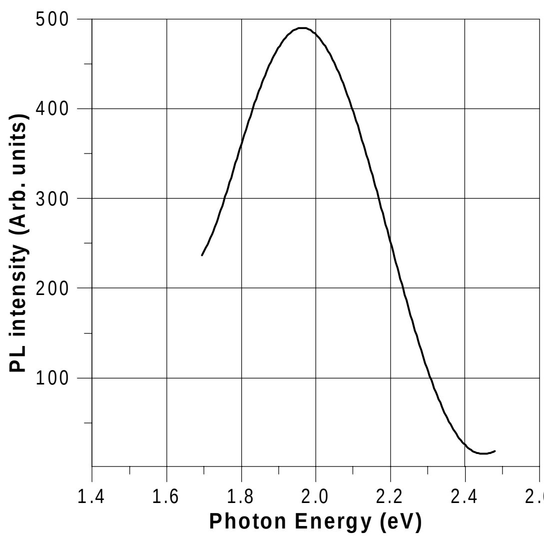

Fig. 2. Typical PL spectrum from a Si-based layer fabricated by the breakdown processing of a silicon by hundreds of laser shots at the same focal spot [the spectrum was taken using 488 nm radiation for pumping].

The formation of layers was attributed to properties of optical breakdown produced by IR radiation. After th generation of first electrons from a silicon target, plasma itself absorbs this radiation through the inverse Bremsstrahlung mechanism and gets heated up to the temperatures of about 10^4 K[2]. We believe that the action of radiation leads to a localized melting and even flash evaporation of the target material. The laser-ablated material and the upper target layer are then heated by the hot breakdown plasma or its currents, leading to additional phase transformations and the initiation of chemical reactions in the plasma. Since the process is pulsed, one can assume recrystallization or local vapo redeposition of the material during the off-times. The combined action of laser- and plasma-related processes leads to a modification of properties of Si-based compounds formed on the target surface and their nanostructuring. It is necessary to note that our studies did not reveal a remarkable redeposition of material on a free target surface, which is typical for conventional pulsed laser ablation with UV radiation [3]. Such a difference of deposition efficiencies is probably connected with quite different mechanisms of radiation absorption in these two cases. In contrast to the infrared light case, the main UV radiation power is absorbed by the target itself and the plasma remains transparent to the oncoming light during the laser pulse. This causes a considerable laser-related ablation of material during the interaction and its redeposition on the free target surface. It is worth mentioning that mechanism of surface treatment in our experiments is similar in many respects to that of the electric spark processing, which was also used for the fabrication of Si-based nanostructured layer [4,5].

However, the origin of 1.9 eV PL is still not clear. Some properties 1.9 eV component enable to attribute it to radiative transitions via non-bridging oxygen hole centers, while other properties give an evidence for a mechanism of radiative recombination between quantum confined states in the nanoscale particles. In any case, a clear identification of the PL mechanism requires further detailed study of mechanical, structural and PL properties of the layers. These investigations are in progress.

In summary, air optical breakdown has been produced on a silicon target for local nanostructuring of its material. Multi-pulse breakdown initiations led to the formation of porous layer under the radiation spot, which consisted of silicon nanocrystals imbedded in silicon dioxide matrix and exhibited strong red PL. The method can be used for a local patterning of photoluminescent nanostructured spots on silicon.

REFERENCES

1. A.V. Kabashin, M. Meunier, “Fabrication of photoluminescent Si-based layers by air optical breakdown near th silicon surface ”, *Appl. Surf. Sci.*, **186**, pp. 578-583, 2002.

2. Yu.P. Raizer *Laser-Induced Discharge Phenomena*, (Consultants Bureau, New York, 1977).

3. A.V. Kabashin, M. Meunier, and R Leonelli, “Photoluminescence characterization of Si-based nanostructured films produced by laser ablation”, *J. Vac. Sci. Tech. B*, **19**, pp. 2217-2222, 2001.

4. R.E Hummel, S-S. Chang**, “**Novel technique for preparing porous silicon”, *Appl. Phys. Lett.*, **61**, pp. 1965-1967, 1992.

5. E.F. Steigmeier, H. Auderset, B. Delley, and R. Morf, “Visible light emission from Si materials”, *J. Luminescence,* **57,** pp. 9-12, 1993.