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Fabrication of photoluminescent Si-based layers by air optical breakdown near the silicon surface

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Abstract

A novel "dry" method for the fabrication of Si/SiO$_x$ nanostructures exhibiting strong visible photoluminescence (PL) is introduced. The method consists in the treatment of a silicon target surface by air breakdown plasma produced by a CO$_2$ laser radiation in atmospheric air. The treatment leads to the formation of a thin porous layer on the silicon wafer, which exhibits a 1.9–2.0 eV PL. Possible mechanisms of nanostructure formation and PL origin are discussed.

Keywords: Optical breakdown; Silicon nanostructures; Photoluminescence

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1. Introduction

Because silicon has an indirect and small bandgap of 1.11 eV at room temperature, it does not emit visible light. However, silicon and Si-based compounds become luminescent in the visible range when they undergo size reduction to the nanometer dimensions [1]. Such a nanostructuring can be produced by a deposition of nanocluster Si-based films through different methods or by the treatment of the silicon surface itself. The luminescent properties give a promise for the creation of silicon-based optoelectronics devices and their integration in standard silicon technology. In this case, "dry" fabrication techniques are of particular interest for these applications due to their good compatibility with silicon processing technology.

A processing of silicon by an electric spark [2–5] is one of the simplest methods for the fabrication of nanostructured layers directly on a silicon wafer. It uses a plasma-based process during which unipolar discharges between two electrodes ionize the gaseous environment and accelerate the generated ions toward the cathode. With a silicon wafer as a cathode, the ions transform the silicon surface to a nanostructured Si-based layer. The processed material was found to exhibit strong photoluminescence (PL) in UV/blue (370–390 nm) and green (520–580 nm) spectral ranges and relatively weak and unstable PL in the red (630–650 nm) range [5]. The method is "dry" and relatively cheap since in the simplest configuration it does not require any vacuum system. However, the method is relatively slow and usually requires several hours of processing to achieve an efficient PL emission.

In this paper, we propose another simple and effective method for the fabrication of photoluminescent silicon structures. We show that PL centers can be formed during the processing of a silicon wafer

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surface by air optical breakdown plasma, produced by focusing a pulsed microsecond radiation from a CO_2 laser near the wafer at air ambient. It is known that the presence of a target lowers the threshold of the breakdown, while after its initiation, the discharge develops in the surrounding air and is maintained by its ionized elements [6]. At this stage, the radiation-related ablation of the target material is almost absent since the air plasma itself absorbs most of the laser power [6]. Such plasma has lifetimes of the order of milliseconds and is characterized by both a high temperature (10^4 K) and the presence of large currents in the range of 10^6 A [7]. We suggest that this plasma can be an effective source for the treatment of silicon surfaces. Structural and PL properties of plasma-treated silicon are examined with an emphasis on visible and near-infrared ranges of the spectrum (S band), which are the most important transitions for optoelectronics applications.

2. Experimental setup

The optical breakdown was produced near a silicon target by the radiation of pulsed TEA CO_2 laser (wavelength 10.6 μm, pulse energy 1 J, pulse length 1 μs FWHM, and repetition rate 3 Hz) as shown in Fig. 1. The radiation was focused by a Fresnel's lens with the focal length of 5 cm, giving the radiation intensity of about 10^8 W/cm^2 at the focal plane.

Standard silicon wafers (N- and P-type, resistances 0.01–10 Ω cm) with dimensions about 1×1 cm^2 were used as targets. They were placed in different positions from $z = -20$ to 20 mm, where $z = 0$ corresponds to the focal plane. For some control tests, an additional Si target was used. It was located near the peripheral part of the air breakdown plasma at $x > 10$ mm as shown in Fig. 1. Since the additional target had a near-parallel orientation with respect to the laser optical axis, it was directly unaffected by the laser radiation itself. Experiments were carried out in atmospheric air (1 atm, 20 °C, 40% humidity). A thin gray-tint layer was formed on the wafer surface after several hundreds shots as a result of the erosion processing.

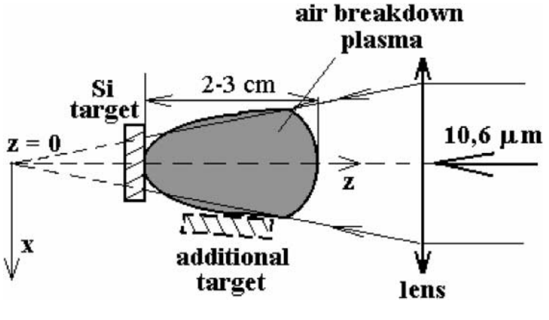

Fig. 1. Schematic diagram of the experimental setup.

For PL measurements, the samples were illuminated by the radiation of a cw Ar^+ laser (model INNOVA 100) with the wavelength 488 nm. The power was 10 mW and the power density was estimated to be 30 W/cm^2. The PL spectra were measured at room temperature using a double spectrometer (model U100, Instruments SA) and a GaAs photomultiplier (Hamamatsu Photonics). The spectra were corrected to take into account the spectral response of the PL setup. Scanning electron microscopy (SEM) was used to examine structural properties of the films. In addition, the surface composition was analyzed by X-ray photoemission spectroscopy (XPS) at a base pressure of 2×10^{-8} Torr using a Perkin-Elmer 5500 system.

3. Results

First of all, we studied the production conditions for the air breakdown plasma. It was found that the radiation intensity was not sufficient to initiate the air breakdown in the absence of the target. However, the placing a silicon target, even at a relatively far distance (10–20 mm) before or after the lens's focal plane, led to an effective plasma initiation. After the breakdown ignition, its intensity raised progressively with the number of laser shots on the same spot and stabilized only after 20–100 shots, corresponding to 10–30 s of treatment. The intensity gain was apparently connected to an appearance of mechanical defects on the target surface, which improved the radiation absorption. Similar breakdown could be initiated by placing another objects such as a copper wire near the focal plane.

The erosion processing by several laser pulses led to a formation of a gray-tint area on the silicon surface, which was in direct contact with air breakdown plasma. The size of this area depended on plasma dimensions, which were mainly determined by the radiation power and the position of the target with respect to the focal plane. Changing this position from

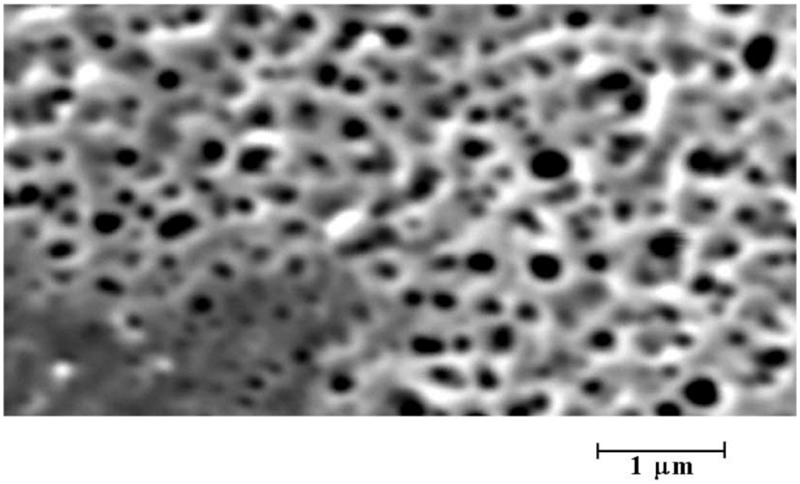

Fig. 2. Typical SEM image of the silicon surface treated by optical breakdown plasma after 10 laser shots.

$z = -20$ to 0 mm, the size of the area could be varied between hundreds of micrometers and several millimeters.

As shown in the SEM image of Fig. 2, the silicon surface treated by several laser shots contained nanoscale holes, between 30 and 150 nm in dimensions. However, smaller pores, not resolved by SEM, may still be additionally present. Prolonged treatment of the silicon surface led to a formation of columns and channels with similar dimensions. Measuring the surface under the holes and channels on the SEM images, we roughly estimated that the porosity of the layers could reach 40–70%. To estimate the thickness of the layers, the samples were cut across the processed area and the side view of the sample edge was analyzed by SEM. Such analysis showed that the thickness of the layers after several pulses could reach 100–500 nm. Maximum thickness was achieved in the center of the processed area, while the layer thickness in peripheral parts of the processed area was less by 20–50%.

Nevertheless, SEM studies did not detect the presence of the ablated material outside the treated area on the free target surface. Similarly, the ablated material was absent on the surface of the additional off-axis target, suggesting that redeposition of target material by conventional laser ablation [8] was almost absent in our experiments. Therefore, the layers with nanoscale holes were mainly formed on silicon surface by its contact with the hot plasma of air elements.

The surface composition of the layers was examined by X-ray photoelectron spectroscopy (XPS). All spectra have demonstrated a single peak at about 104 eV, which is always assigned to 2p photoelectrons of pure SiO_2, suggesting that the upper surface layer mainly consisted of silicon dioxide.

The samples treated by air breakdown exhibited strong PL signals, which could be easily seen by naked eyes. Fig. 3 shows that a typical PL spectrum from the

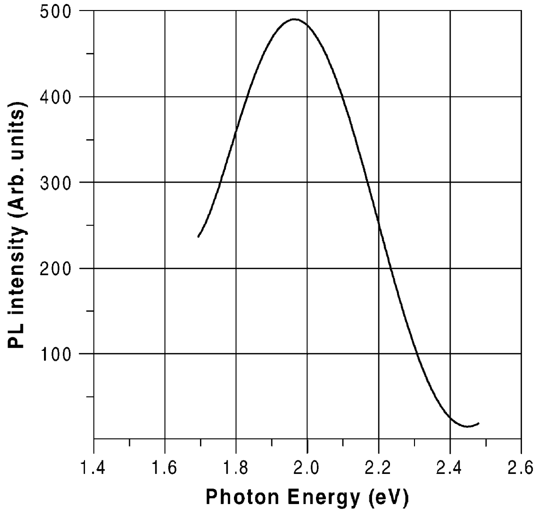

Fig. 3. Typical PL spectrum from silicon surface treated by the breakdown.

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-type) and doping level.

4. Discussion

It is accepted that the optical breakdown can be divided approximately into three successive phases [6]. During the initial breakdown of the first phase, the ionization develops in a cold gas and an initial plasma appears. The presence of a solid target or aerosol particles near the focal plane of the lens enables to lower the intensity threshold of air optical breakdown by 2–3 orders of magnitude by generating the initial electrons. The second phase is characterized by the interaction of the 1 μs laser pulse with the plasma already formed. The plasma, consisting mainly of air elements, absorbs the laser radiation through the inverse Bremsstrahlung mechanism and thus gets heated up to the temperatures of about 10^4 K. Finally, a gradually decaying shock wave or ‘‘fireball’’ appears after the laser pulse, which can live several milliseconds and is characterized by an intense light emission and a generation of electromagnetic fields [9–11] and ultra-strong currents [7].

Based on similar properties of the electric spark treatment of silicon [2–5] and on the basic mechanism of the optical breakdown, we propose that the light action and contact of a silicon surface with the plasma, heated to high temperatures (10^4 K) and presenting intense currents (10^6 A), lead to a localized melting and even flash evaporation of the target material. Since the plasma is pulsed, one can assume recrystallization of the material or vapor redeposition on the wafer-free surface during the off-times. All these mechanisms may lead to a formation of nanostructured $Si–SiO_x$ complexes exhibiting visible PL.

Generally speaking, the generation of 1.9 eV PL band is a common feature found in damaged silicon oxides, which were exposed to X-ray radiations [12]. This emission is usually ascribed to radiative transitions via non-bridging oxygen hole centers [13]. However, detailed analysis of similar 1.9 eV signals and their properties in the case of spark-processed silicon does not confirm this assumption [4,5]. Another mechanisms cannot also be ruled out. For example, some properties of the 1.9 eV from spark-processed silicon [3] gave an evidence for a mechanism of radiative recombination between quantum confined states in the nanoscale particles [1]. In any case, a clear identification of the PL mechanism requires further detailed study of mechanical, structural and PL properties of the deposited and annealed films. These investigations are in progress.

Properties of the layers in our experiments are similar in many respects to the films produced by electric spark processing, where ion bombardment of silicon surfaces is proposed as the main mechanism for the surface treatment [2–5]. They also contained holes and pores with dimensions of about 10–500 nm and mainly consisted of silicon dioxide [2]. In addition, detailed study of the structure of these layers by transmission electron microscopy revealed the presence of many nanometer-size silicon crystals embedded in SiO_2 matrix [4]. The spark-processed layers also exhibited 1.9 eV PL. However, in contrast to our studies, these 1.9 eV signals were unstable and relatively weak in comparison with other peaks in the green (2.35 eV) and ultraviolet ranges [5].

5. Conclusion

The plasma of air optical breakdown has been used for the first time for the silicon surface treatment. The processed area had a porous structure with nanoscale holes and exhibited strong red PL. The obtained material may be used for optoelectronics applications. Detailed study of the influence of different processing parameters on material properties and further characterization of the layers are being performed and will be the subject of another publication.

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