Available online at www.sciencedirect.com
ScienceDirect
Nuclear Instruments and Methods in Physics Research B 266 (2008) 2576–2580
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Luminescent nanoclusters array fabricated by pulsed laser beam irradiation

Brijesh Kumar, R.K. Soni *

Laser Spectroscopy Laboratory, Physics Department, Indian Institute of Technology Delhi, New Delhi 110 016, India

Received 20 February 2008
Available online 28 March 2008

Abstract

Ordered luminescent nanoclusters array in the form of grating structures are fabricated on silicon (100) surface by Q-switched Nd:YAG laser beam irradiation of second harmonic wavelength (532 nm) in vacuum. Blue-green photoluminescence (PL) spectrum from the ordered nanoclusters array exhibits two asymmetrical peaks at 2.58 eV and 2.88 eV in the blue-green region corresponding to the bimodal distribution of nano size clusters. The size of the nanoclusters is estimated from the three dimensional quantum-confined model incorporating Gaussian size distribution. When subjected to rapid thermal annealing at 710 °C for 10 min in N_2 atmosphere there is an enhancement of the PL intensity without any change in the peak emission energy and broadening suggesting that the origin of PL is related to quantum confinement effect in Si nanocrystallite. The surface morphology of the irradiated surface varies considerable with the number of laser shots, laser fluence and ambient conditions.

PACS: 61.80.Ba; 68.35.Bg; 61.46.w; 61.82.Fk; 78.55.Ap

Keywords: Pulse laser irradiation; Silicon; Nanoclusters array; Surface morphology; Photoluminescence

1. Introduction

Since the discovery of visible photoluminescence at room temperature from nanocrystalline silicon, there has been rapid progress in the controlled growth of nanometer size structures and their applications in photonics. Silicon based photonics require tailoring of electronic band structure for wavelength tunability and large excitonic emission. Laser processing has long been used for annealing of structural disorder and surface modifications in semiconductors. Moreover, pulse laser processing has emerged as an important tool for micro/nano structures fabrication on the surface of semiconductors. The pulsed laser irradiation on materials at low laser energy density, typically less than 1 J/cm^2, produces a gradual change in the surface topography which transforms into well-defined laser induced periodic surface structures (LIPSS) caused by the interference of the incident beam with surface scattered wave from the surface disturbance [1–3]. The LIPSS have been extensively investigated on different materials by a number of workers for over two decades using low power cw laser [4], nanosecond [5,6] and femtosecond [7,8] lasers covering the wavelength range from 0.249 μm [9] to 10.6 μm [10]. Many authors have observed the formation of well-defined periodic structures on the surface of metals, ceramics, polymers and semiconductors [7,11–13]. The mechanisms for the formation of the LIPSS have attracted extensive research efforts. The LIPSS formation is attributed to interference between the incident beam and scattered beam parallel to the substrate surface [10], induced polarization charge on defects boundaries [14], holography recording of surface polaritons due to surface defects [15], surface waves due to surface roughness and inhomogeneity [16], freezing of capillary waves [3] and transient periodic heating pattern [17]. It is generally accepted that the ripple

* Corresponding author. Tel.: +91 11 26591304; fax: +91 11 26581114.
E-mail address: ravisoni@physics.iitd.ernet.in (R.K. Soni).

0168-583X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2008.03.194

structures is formed by interference between the incident laser light and some form of induced surface wave [10]. Surface waves may propagate along the interface between the crystal and vacuum [18,19], if dielectric constant of the crystal satisfy $\varepsilon(\omega) = 1 - \omega_p^2/\omega^2 \leqslant 1$, where ω and ω_p are the laser and plasma frequencies, respectively. Laser induced ripples formation is promising for fabrication of surface gratings, shallow junction of metal–oxide–silicon transistors and would be used to roughen the surface of micro electro mechanical systems (MEMS) components to enhance the surface adhesion and improve the performance or life time of micro-devices. In addition, ripple structures have a variety of potential applications where increased surface area is desired such as chemical and gas sensing applications.

Many different mechanisms have been proposed to explain the visible PL from nanocrystalline silicon. Some workers suggested that surface hydrides or Si–O–Si complexes might play a role of radiative recombination centers in the silicon nanostructures [20–22]. The radiative recombination through the localized states inside the SiO_x $(0 < x \leqslant 2)$ oxide shell surrounding the silicon core or on the Si–SiO_x interface has also been proposed [23–27]. In addition, surface states can play a dominant role in photoluminescence emission. Most commonly accepted mechanism of light emission, however, is the quantum confinement effect (QCE) in nanocrystalline silicon [28–33] and accounts for observed blue shift for smaller size.

We have fabricated ordered luminescent nanoclusters arrays on silicon (100) surface by Q-Switched Nd:YAG laser beam irradiation of second harmonic wavelength (532 nm) in vacuum. Blue-green photoluminescence (PL) spectrum is obtained from the ordered nanoclusters array. The effect of rapid thermal annealing on the PL emission is studied. Further, the morphological changes with number of laser shots, laser fluence, in ambient conditions and conductivity of the silicon substrate are investigated (see Table 1).

2. Experimental

The substrates were arsenic doped n-type and boron doped p-type silicon (100) oriented with resistivity 1–10 Ω cm, thickness 400 μm and doping concentration $9 \times 10^{14}/cm^3$ and $2.5 \times 10^{15}/cm^3$, respectively. Laser irradiation was carried out using second harmonic wavelength (532 nm) of Nd:YAG laser at pulse repetition rate (PRR) of 10 Hz, pulse width 5 ns, and energy density in the range of 300–700 mJ/cm^2 in air, or flowing Cl_2 gas or in vacuum of base pressure 10^{-3} torr. The nanoclusters array was subjected to rapid thermal annealing at temperature 710 °C for 10 min in N_2 ambient to remove defects from the irradiated surface. For PL measurement 240 nm (5.16 eV) wavelength of a Xenon lamp was used for excitation. Morphological changes were investigated using SEM.

3. Results and discussion

Fig. 1(a) shows SEM image of linear ordered nanoclusters array fabricated on the p-silicon (100) surface at the base pressure of 10^{-3} torr and laser energy density of 305 mJ/cm^2 irradiated with 15,000 laser pulses. The nanoclusters are aligned in the form of grating like structure. The ordering of the surface nanoclusters depends on pressure inside the chamber and the laser pulse energy. The spacing between the aligned nanoclusters is 0.65 μm, for the incidence angle of 11°. The period and orientation of these surface structures has been shown to depend on the laser polarization, angle of incidence, wavelength, irradiation time and energy density. The interaction of intense pulsed laser irradiation with silicon excites the surface plasmon wave and the highly ordered grating like surface structure is caused by the optical interference of the incident laser beam with the scattered beam traveling very nearly along the surface with a velocity equal to or close to the velocity of light in free space. Periodic structures have been observed in pulse laser annealing of silicon surface due to the photothermal effect. In our case the incident laser frequency $\omega = 3.543 \times 10^{15}$ Hz is slightly less than the plasma frequency ($\omega_p = 2.48 \times 10^{15}$ Hz) for a single laser pulse on the silicon surface, therefore, the condition for the surface wave excitation $\varepsilon(\omega) \leqslant -1$ is not fulfilled. However, under large number of pulse irradiation the nonequilibrium density of charge carriers and refractive index variation provide suitable condition for the surface plasmon–polariton wave propagation. No periodic structure was observed when the number of laser shots was below 15,000. On the other hand, irradiation on n-type silicon surface yield periodic structures at much lower number of laser shots of 9000 under identical experimental condition, as shown in Fig. 1(b). Clearly, the formation of periodic structure in vacuum and resulting surface morphology also depends on substrate conductivity and the type of charge carriers of silicon substrate.

The interaction of intense photon beam with solid surface causes photothermal effects leading to phase changes and surface melting of the irradiated region. In some instance induce surface tension can cause physical ablation to form microholes/microcone as a result of laser heating [34]. It has been observed that microcones are formed only when microscopic holes are already present on the surface. Laser irradiated microstructures usually do not have sharp

Table 1
Best fitting parameters of PL spectrum with two peaks

R_{01} (Å)	R_{02} (Å)	σ_1 (Å)	σ_2 (Å)	PL_1 peak (eV)	PL_2 peak (eV)	FWHM (meV)
5.9	6.2	0.7	2.32	2.58	2.88	590