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Two mechanisms of nanocrystals formation under ion irradiation of silicon

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Abstract

The irradiation of silicon surface with ions results in the appearance of photoluminescence (PL) properties which are characteristic of Si nanocrystals. Two fluence ranges are considered – low fluence region, LFR (near the amorphization threshold) and high fluence region, HFR. For the LFR, the PL appears after annealing at ~300 °C, whereas for the PL at HFR, the annealing is not required. It is suggested that PL for LFR is associated with nanocrystalline regions remaining in the amorphous layer. The computer algorithm is elaborated for the calculation of fluence kinetics of nanostructure evolution which provides qualitative agreement with experimental PL fluence dependence. For the HFR, another model is suggested which relates the formation of nanocrystals beneath the amorphous layer with driving self-interstitial atoms (recoils) into the depth. The strong inhomogeneous mechanical stresses caused by this process leads to the nanofragmentation of the structure in the deep interstitial-enriched layer of silicon.

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1. Introduction

The production of nanocrystalline silicon is very important due to their useful optical and electrical properties. Particularly, massive silicon has poor light-emitting properties due to its non-direct band structure. Whereas, the nanocrystalline Si enables by luminescence in red/near-infrared region of spectrum that makes this material promising for optical and optoelectronic applications. Many methods have been elaborated for the formation of Si nanocrystals. The majority of the methods are very complicated and time-consuming. Earlier, we suggested simple and comparatively expressive method which consists in the irradiation of silicon surface with ions of medium energy [1]. It appears that, in some fluence interval which is close to amorphization threshold, the silicon acquires ability to photoluminescence in red/near-infrared region of spectrum (700–1000 nm) at room temperature [2]. This property was interpreted [2] as being associated with nanostructuring of silicon by ion irradiation. Indeed, the ion irradiation results in amorphization of subsurface layer. In some fluence interval near the amorphization threshold, crystalline regions should remain in amorphous layer and they can serve as quantum dots in a confining matrix. As an example, the PL spectra for silicon irradiated with Ar^+ (150 keV) at various fluences are presented. The samples were post-annealed at 300 °C in order to reduce the number of dangling bonds – centers of non-radiative recombination. The PL was measured at room temperature under excitation with Ar laser (488 nm). Two PL bands were observed (Fig. 1). One of them (at ~750 nm) was ascribed to nanocrystals, another (at ~1000 nm) to amorphous phase [2]. The PL intensity firstly increases with fluence, and then it falls down (Fig. 2), what was expected (at least, for the peak at ~700 nm).

Another fluence region where intensive PL was observed (with nearly the same positions of spectral maxima as for

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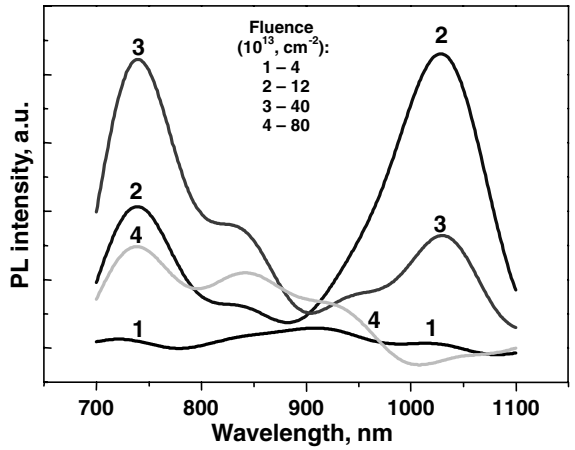

Fig. 1. The photoluminescence spectra of silicon irradiated with Ar^+ (150 keV) at different fluences (LFR). The post-annealing at 300 °C.

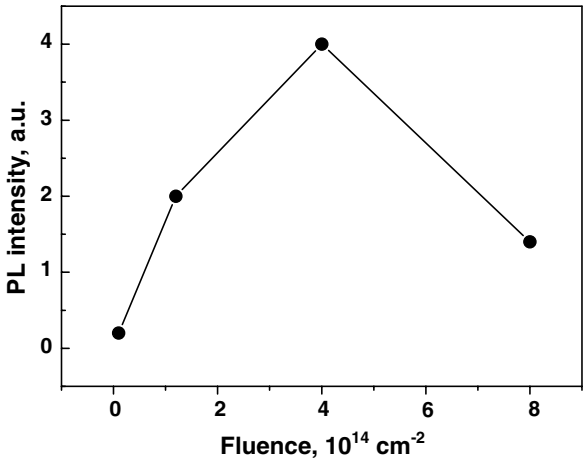

Fig. 2. The fluence dependence of photoluminescence intensity for Si irradiated in the same regimes as for Fig. 1 (the maximum at ~750 nm).

LFR) respects to much higher irradiation fluences with ions of inert gases – "high fluence region" (HFR). The characteristic feature of HFR is the retaining the PL after etching off the layers which are much thicker than the ion ranges ($R_p + \Delta R_p$) [3]. The surface topography study by AFM method reveals the appearance of blisters for these fluences.

In this paper, we present the model and algorithm for computer calculation of nanostructural evolution in the LFR and the qualitative model of nanostructuring by ion irradiation in the HFR.

2. The calculation of nanostructural evolution in the LFR

The following simplified model [4] of defect accumulation and of structural evolution in the LFR was used. The amorphous phase forms as a result of the accumulation of point defects as soon as their concentration in a given local volume reaches the critical magnitude (~10 at.%). For the simplicity, we will take here into account only vacancies and divacancies. The latter are formed by the coagulation of the vacancies (meeting with each other during their diffusion) which are mobile at room temperature. The vacancies take participation in two processes: the loss due to the trapping by unsaturating traps (impurities, dislocation, etc.) and coagulation into divacancies. The following parameters were adopted for the calculation [4]: vacancy diffusion coefficient $D_v = 5 \times 10^{-10}$ cm^2/s; energy barrier for vacancies coagulation $E_{vv} = 0.24$ eV; trap concentration $N_t = 2 \times 10^{18}$ cm^{-3}; the energy barrier for vacancy trapping $E_{tv} = 0.06$ eV.

As the ion fluence increases, some regions are transformed into amorphous state, the number and sizes of amorphous region increase and at some fluences nearly continuous amorphous layer with crystalline inclusions forms. At further fluence increase, the sizes of such inclusions diminish and approach the nanometer values; their number increases first and then decreases (eventually, the full amorphization of surface layer occurs).

The algorithm of the computer calculation is as follows:

- the model volume is divided into the cells (typically, 2×2 nm^2);
- the TRIM code [5] is used for the modeling displacement cascade produced by the first ion;
- the calculation of the number of vacancies and divacancies in each cell for the time of the second ion incidence is performed;
- the same calculation is performed for the time of the third ion incidence, etc.;
- the cells for which the total number of defects became equal to the given value (10 at.%) are registered as "amorphous" ones;
- the total area of amorphous regions for cross section of model volume at a given depth is calculated;
- the mean sizes and number of the regions non-amorphized yet are registered as the functions of the fluence.

The coordinates of incidence points for each ion and the time intervals between the ion incidences are determined by

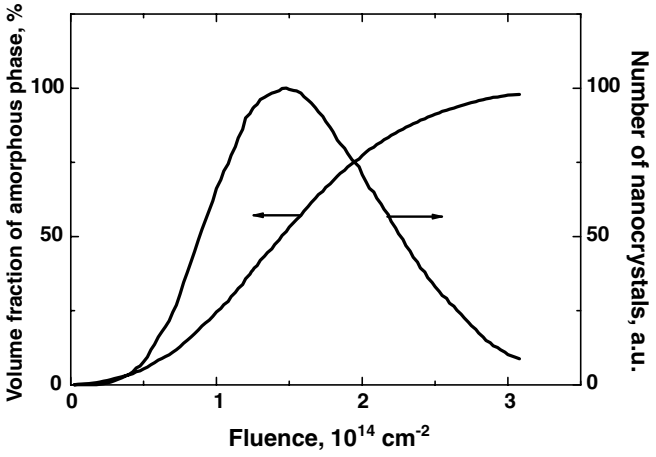

Fig. 3. The calculated fluence dependence of volume fraction of amorphous phase and the number of nanocrystals for irradiation of silicon with Ar^+ (50 keV). The depth is equal to R_p. The current density is 10 μA/cm^2.

Monte Carlo procedure for a given fluence rate (current density) magnitudes. The kinetics of amorphous phase accumulation and accumulation of crystalline nanoinclusions with sizes $d < 10$ nm at the depth of R_p for Ar^+ (50 keV) are presented on Fig. 3. It is seen that the number of the nanocrystals changes with fluence in non-monotonous manner. This behavior is in a qualitative agreement with experimental fluence dependence of PL (Figs. 1 and 2) that evidences in favor of the correctness of our model. The quantitative agreement can be improved if one takes into account inhomogeneous depth distribution of damage and provides some fitting of parameters used at calculation.

3. The model of nanostructure formation in the HFR

As the PL at HFR has nearly the same spectrum feature as for LFR, we can assume that sources of PL also are similar. The HFR respects to the fluences for which the continuous amorphous layer (without crystalline inclusions) should exist. Hence, the light-emitted nanocrystals are likely localized beneath the amorphous layer. This is evidenced also by the fact that PL is observed after the amorphous layer is already etched off. How can one explain the appearance of nanocrystalline structure at such depths?

Recently, the mechanical model of amorphization under ion irradiation was suggested by us [6]. According to this model, the inhomogenously distributed stresses caused by radiation damage are resulted in fragmentation of monocrystalline structure. The main features of this model (with some modification) can be used also for the case of the nanocrystal formation beneath of amorphous layer (at large fluences).

While at the depths comparable with ion ranges ($R_p + \Delta R_p$), the radiation defects are formed directly in the displacement cascades, for larger depths, the defects – self-interstitial silicon atoms can penetrate due to the transport via driving in (recoiling) by manifold incidence of ions (overlapping many displacement cascades).

According to the model [6], the amorphous phase is formed through the rotation of the small ($\leqslant 1$ nm) "blocks" of initially crystalline phase by some arbitrary (generally, large) angles. In contrast, the formation of *nanocrystalline* phase can occur through the "block" rotation by not only large angles but by small ones, too. In this case, the sizes of crystalline blocks should be larger (2–5 nm) than for amorphization process. The intercrystallite potential barriers (required for quantum confinement of electrons, i.e. for the behavior of nanocrystals which is characteristic of quantum dots) can be provided by amorphous SiO_x shells around the individual nanocrystals. For the formation of such shells, the oxygen can be delivered through the recoil of the atoms from the sample surface.

It is believed that, during inert gas implantation, the sites of Si atoms transported into the large depths are substituted by inert atoms which then form the blisters. If the sputtering is small (as is true for not too heavy ions, e.g. Ne^+), the net volume of blisters should be nearly equal to that of the displaced Si atoms localized now beneath the amorphized layer. This permits to evaluate the number of such atoms from the observed blister topography obtained by AFM method. The results of such evaluation and comparison with the calculations of the number of displaced atoms will be done later.

4. Conclusions

The models of silicon nanostructuring by ion irradiation are presented for two fluence intervals – low and high fluences (LFR and HFR, respectively). These models are elaborated for the interpretation of the photoluminescence properties of ion irradiated layers which were observed earlier. For LFR, the result of calculations (based on simplified model of radiation defect accumulation) agrees qualitatively with experimental fluence dependence of the photoluminescence. For HFR, the presented here model also qualitatively agrees with experimental data. However, it has to be further developed yet in a quantitative manner.

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