FORMATION OF LUMINESCENT NANOCRYSTALLINE SILICON FILMS FROM A-SI:H BY USING RAPID THERMAL ANNEALING AND WET CHEMICAL ETCHING

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Nanocrystalline silicon films, which exhibit efficient photoluminescence, were formed from amorphous films of hydrogenated silicon subjected to rapid thermal annealing and stain etching in hydrofluoric acid based solutions. The samples were investigated by means of scanning and transmission electron microscopy, optical spectroscopy of reflection, Raman scattering and photoluminescence methods, which revealed the nanocrystalline structure and excellent optical quality of the formed nc-Si films.

Introduction

Research interests in all silicon (Si)-based light-emitting diodes for next-generation Si photonic devices are stimulated by observation of efficient light emission in Si nanocrystal (nc-Si) (see for examples Refs. [1-3]). Recently it has been demonstrated that thin films of nc-Si with efficient photoluminescence (PL) in visible spectral range were formed by wet chemical etching (stain etching) of microcrystalline Si deposited by plasma-enhanced chemical vapor deposition (PECVD) with a flow of silane gas that is highly diluted in hydrogen [4]. When the silane concentration in the mixture is relatively high the films of hydrogenated amorphous silicon (a-Si:H) are usually formed [5]. On the one hand, it is known that the stain etching of a-Si:H did not result in formation of luminescent films [1]. On the other hand, a-Si:H can be crystallized by using annealing procedure as rapid thermal annealing (RTA) [6], and then the crystallized films can be used to prepare nc-Si with efficient PL. The luminescent films of nc-Si by RTA of silicon-rich silicon suboxides prepared by PECVD [7] and magnetron-assisted sputtering [8] were demonstrated. Usually, the RTA treatment of a-SiH is accompanied by losses of the hydrogen content in the films, which result in a deterioration of their electronic and optical properties [9].

The electronic properties of nc-Si samples are obviously dependent on RTA parameters, which influence the sizes of Si crystallites and defect density on crystallite boundaries. Therefore the residual defects in nc-Si after RTA have to be passivated. We report the preparation of nc-Si films, which exhibit efficient PL, by using RTA of a-Si:H combined with stain etching (SE) in HF-based solution.

Experimental

Plasma-enhanced chemical vapor deposition or magnetron reactive sputtering were used to depose thin (thickness of about 0.5-1 □m) films of a-Si:H on quartz substrates. Then deposited films were subjected to a conventional RTA using a tungsten halogen lamp. A single-pulse cycle was set to increase the temperature from room temperature to 900-950 C and back. The total annealing time was varied from 10 to 50 s. The RTA-treated films were then subjected to the SE-procedure in aqueous solutions of $HF:HNO_3$=100:1 or $HF:FeCl_3:H_20$=1:2:2 for time varied from 1 s to 15 min.

The initial a-Si:H films, RTA- and RTA+SE-treated films were investigated at room temperature by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible–near-infrared (UV–VIS–NIR) absorption/reflection measurements, Raman spectroscopy and photoluminescence methods. SEM studies were carried out by using a LEO 1455 Carl Zeiss electron microscope. TEM analysis was done with a LEO 912 AB Omega electron microscope. The Raman scattering measurements were made using a LabRAM HR 800 microRaman

spectrometer with an Ar-laser at wavelength of 488 nm for the excitation. A Perkin-Elmer UV–VIS–NIR spectrophotometer was used for the transmittance and reflectance measurements in the spectral range from 200 to 1100 nm. PL was excited by a N_2-laser (wavelength 337 nm, pulse duration 10 ns, repetition rate 100 Hz). The PL signal was dispersed by a 50 cm monochromator and was detected by a charge-coupled-device in the spectral range from 350 to 1100 nm.

Results and discussion

Fig. 1 show typical SEM image of nc-Si film prepared by RTA followed by stain etching. Both micro- and nano- structures observed in SEM pictures of the prepared samples are indicative for heterogeneous structure transformations in the films. These transformations are initiated by heating under RTA and local electrochemical reactions related to the stain etching process. The latter include obviously formation of nanopores because of stain etching of Si in HF-based solution [10].

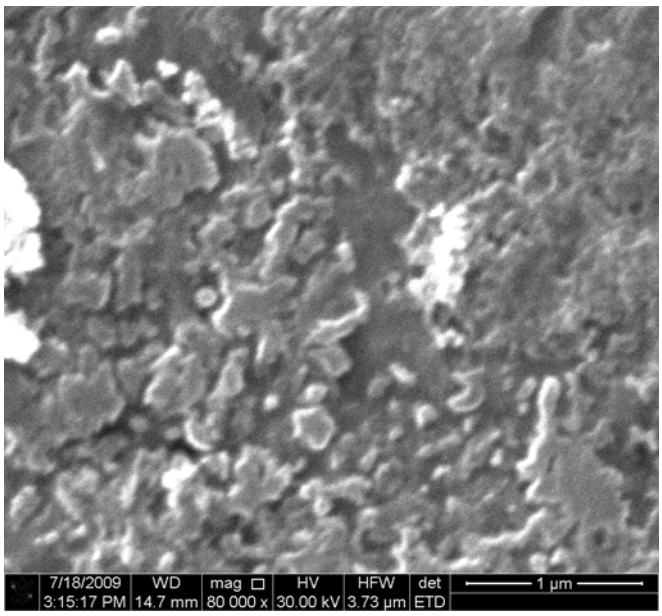

Fig. 1. Typical SEM image of nc-Si film obtained from a-Si:H by using RTA and stain etching

According to TEM investigations the RTA treated films were partially crystalline with typical sizes of nc-Si of about 5-10 nm. The porous structure of the samples subjected to the stain etching was also detectable in their TEM images. For example, a TEM micrograph for the sample after RTA (900 ^{o}C for 50 s) followed by stain etching in HF:$FeCl_3$:H_20=1:2:2 for 10 min is presented in Fig. 2. It is worth to mention that the RTA processing with longer times lead to better crystalline quality and larger nanocrystal size in the formed nc-Si films.

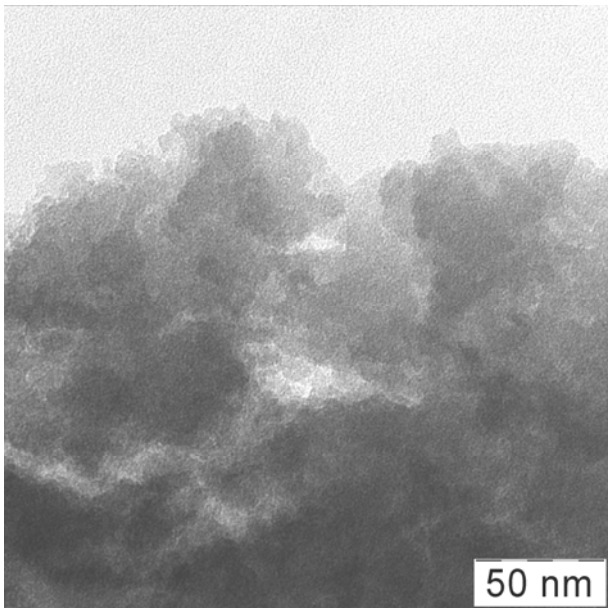

Fig. 2. TEM micrograph of nc-Si film subjected to RTA and SE. The inset shows the electron diffraction pattern

The UV–VIS–NIR analysis of the RTA-treated a-Si:H films reveals the strong reflection bands at 274 and 368 nm, which confirms the crystallization of silicon in the films (see Fig.3). The interference patterns in the VIS–NIR ranges of the reflection spectra indicate high optical quality of the RTA-treated films and those subjected to the post-etching. Because of the porous structure of the formed nc-Si films their average reflectance was lower than that for c-Si.

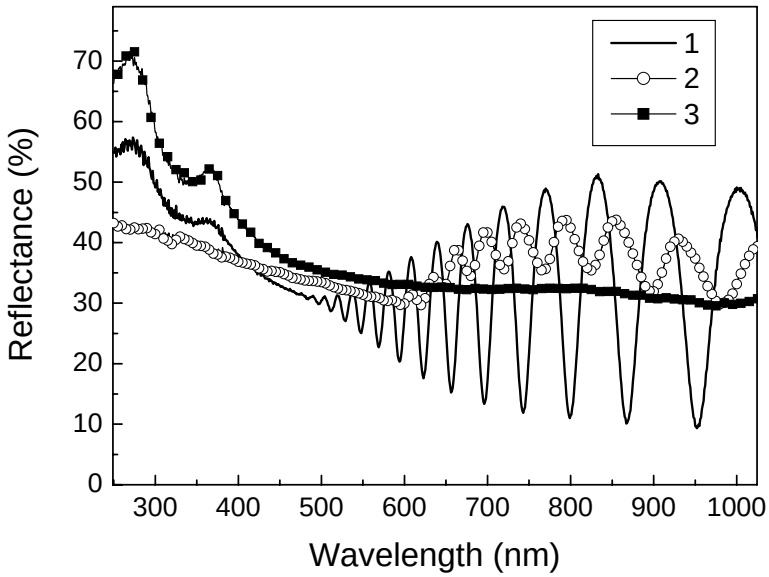

Fig. 3. Reflection spectra of a nc-Si film obtained from a-Si:H by using RTA and stain etching (1) as well as the spectra of initial a-Si:H film (2) and c-Si wafer (3) for comparison

As it is shown in Fig.4 the Raman spectrum of initial a-Si:H film is represented by a broad line at 480 cm^{-1}, which is typical for amorphous Si. The Raman spectra of the formed nc-Si films consist of a line at 513-519 cm^{-1}, which is shifted to low frequency range in respect to the spectrum of c-Si-substrate (520.5 cm^{-1}). The shift is explained by the phonon confinement in Si nanocrystals with sizes of 2-8 nm [11,12]. The volume fraction of nc-Si in RTA-treated films estimated from the analysis of the Raman spectra [8] was typically about 50-90% and it increases further after SE-procedure. Note, the stain etching in HF:HNO_3 even for short times about 5 sec resulted in nearly complete losses of amorphous Si phase, while the SE-treatment in HF:$FeCl_3$:H_20 for at least 10 min did not removed residual a-Si:H (compare curves 1 and 2 in Fig.4). It can be explained by slower dissolution rate in the latter solution [4].

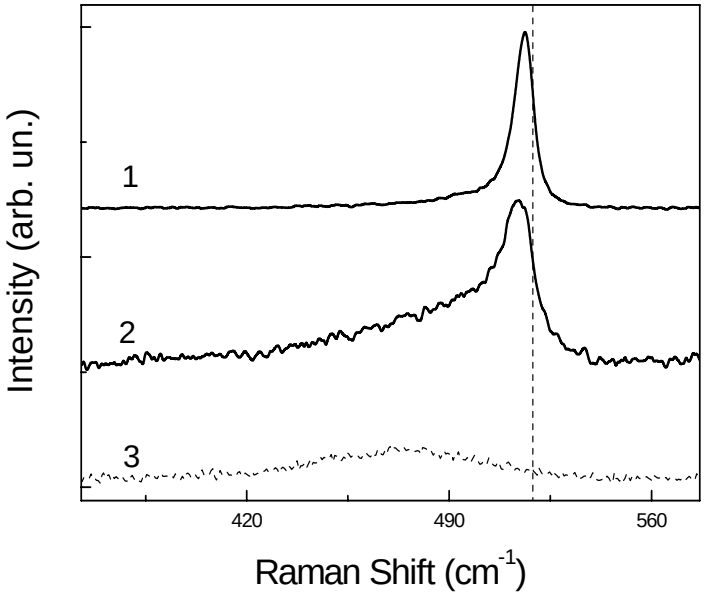

Fig. 4. Raman scattering spectra of the nc-Si film obtained from a-Si:H by using RTA at 950 ^oC for 40 sec and SE in HF:HNO_3 for 5 sec (1) or in HF:$FeCl_3$:H_20 for 10 min (2), as well as, for comparison, the spectrum of the initial a-Si:H film (3)

The PL measurements did not revealed any remarkable PL from as-prepared a-Si:H films as well as from the RTA-treated samples without SE-procedure. The intensive PL in the spectral range of 550-950 nm was observed for the RTA-crystallized films subjected to the SE-treatment (see Fig.5). The PL intensity, spectral position and lifetime of the post-etched nc-Si films were similar to those measured for stain-etched porous Si formed from a c-Si wafer in the same solution [10]. Similarly to anodized porous Si the observed PL of the SE nc-Si films can be attributed to radiative recombination of excitons confined in hydrogen passivated nc-Si [13]. Note, that no PL was observed from the films of a-Si:H post-etched in the same solution. It means that the formation of nc-Si is crucial for the efficient PL of the SE-treated films.

The PL spectra of nc-Si films prepared from a-Si:H by using RTA at 950 ^oC for 40 sec and SE in different solutions are presented by curves 1 and 2 in Fig.5. The PL Intensity of the nc-Si film after SE in HF:HNO_3 was lower than that for the sample treated in HF:$FeCl_3$:H_20 solution. Similarly to the PL data obtained for porous Si electrochemically prepared n HF:HCl mixtures [14] this fact can be explained by better passivation of Si nanocrystals in the solution with oxidized chlorine ions. The

stronger PL of the nc-Si films after SE in HF:$FeCl_3$:H_20 correlates with the observation of residual amorphous Si phase by the Raman spectroscopy (see Fig. 4). The both observations can be explained by slower rate of the dissolution of Si in HF:$FeCl_3$-based solution in comparison with the HF:HNO_3 mixture. The observed stronger PL intensity of the samples treated in HF:$FeCl_3$-based solution agrees with the PL data reported for the microcrystalline Si films prepared by PECVD [4].

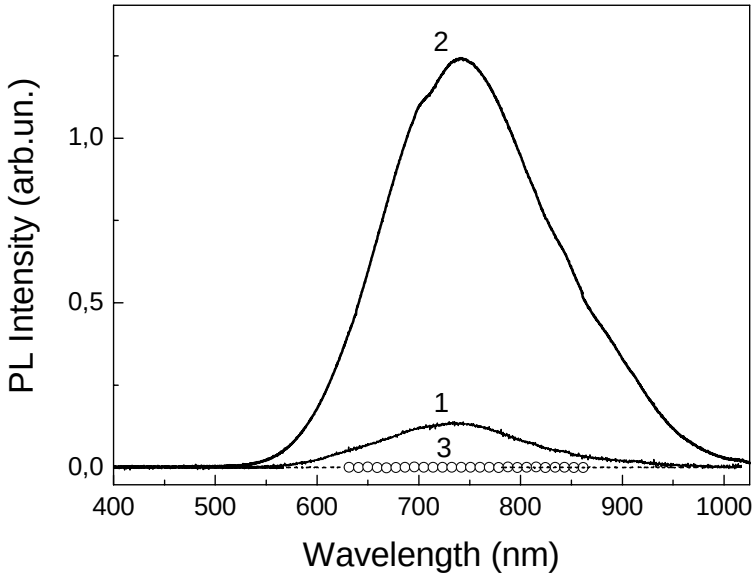

Fig.5 PL spectra of a nc-Si film obtained from a-Si:H by using RTA at 950 ^oC for 40 sec and SE in HF:HNO_3 (1) or HF:$FeCl_3$:H_20 (2), as well as, for comparison, the spectrum of the initial a-Si:H film (3)

In conclusions, the films of nc-Si with efficient PL were formed from a-Si:H films by combining RTA and stain etching procedures. The prepared samples were investigated by means of the electron microscopy and optical spectroscopy. The obtained results demonstrate that the fast procedure of RTA followed by wet chemical etching can be used to obtain nc-Si-films with desired optical properties.

Acknowledgements

We are grateful to Dr. S.A. Abramchuk for the TEM measurements. The optical measurements were done by using equipment of the Center of User's Facilities of the Physics Department of M.V. Lomonosov Moscow State University. The work was partially supported by the Ministry of Education and Science of the Russian Federation (contract #02.513.12.3058).

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ЖУҚА АМОРФ КРЕМНИЙДІ ҚЫЗДЫРЫП ЖӘНЕ ҚЫШҚЫЛДАРДА СӘЛІ ЕРІТІП, ЛЮМИНИСЦЕНЦИЯЛЫҚ НАНОКРИСТАЛДЫ ЖУҚА ҚАБЫРШАЛАР ЖАСАУ.

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Жуқа аморф кремнийді қыздырып және қышқылдарда сәлі ерітіп, фотолюминисценциясы жоғары нанокристалды жуқа кабыршықтар жасалынды. Осы қабыршықтар беткі және өтү микроскопия, шағылу оптикалық спектроскопия, Раман спектроскопия және фотолюминисценция әдістерімен зерттелінді. Зерттеулер нәтіжесінде наноқұрылымды кабыршықтардың жоғары оптикалық қасиеттері дәлеленді.

ФОРМИРОВАНИЕ ЛЮМИНЕСЦЕНТНЫХ НАНОКРИСТАЛЛИЧЕСКИХ ПЛЕНОК КРЕМНИЯ ИЗ a-Si:H МЕТОДОМ БЫСТРОГО ТЕРМИЧЕСКОГО ОТЖИГА И ХИМИЧЕСКОГО ТРАВЛЕНИЯ

Е.Т. Таурбаев, В.Ю. Тимошенко, Н.Е. Маслова, К.А. Гончар, К.К. Диханбаев, В.Е. Никулин, Е.А. Сванбаев, Т.И. Таурбаев

Нанокристаллические пленки кремния с высокой эффективностью фотолюминесценции изготовлены быстрым термическим отжигом и окрашивающим травлением в растворах на основе плавиковой кислоты. Эти пленки исследованы методами сканирующей и просвечивающей микроскопии, спектроскопии отражения, Рамановской спектроскопии, фотолюминесценции и показали нанокристаллическую структуру и высочайшее оптическое качество.