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FABRICATION AND CHARACTERIZATION OF THE SIZE-CONTROLLED AND PATTERNED nc-Si DOTS*

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A new method of phase-modulated excimer laser crystallization is adopted to fabricate the patterned nanometer-sized crystalline silicon (nc-Si) dots within the sandwiched structure (a-SiN_x:H/a-Si:H/a-SiN_x:H) films. The results of transmission electron microscopy, electron diffraction and Raman scattering show the ultra-thin and single-layer nc-Si films were patterned in the lateral direction and the size of crystallites is controlled by the thickness of as-deposited a-Si film in the longitudinal direction. The effects of the laser energy density on the structures of the samples and the crystallization mechanism are discussed.

Keywords: nanocrystalline silicon, constrained crystallization, laser-induced crystallization, sandwiched structure

PACC: 7280N, 6890, 7865

I. INTRODUCTION

Though silicon lies at the heart of contemporary microelectronics, its small and indirect band gap yields extremely low efficiency of infrared emission, hampering its further application in optoelectronic devices. In the process of searching for more efficient silicon-based optoelectronic materials, a usual way is trying to fabricate lower dimensional and nanometer-sized Si materials. In the last few years, some groups reported quantum effects in nc-Si, such as a blue shift of the optical band gap,[1] visible photoluminescence[2] and electroluminescence.[3] as well as resonant tunneling.[4] These properties are expected for the applications in optoelectronics and nano-electronics. But there are few papers on how to precisely control the size of Si crystallites.[5]

In our previous work, we proposed a method of laser-induced constrained crystallization of ultra-thin hydrogenated amorphous silicon layers within a-Si:H/a-SiN_x:H multilayers to fabricate nc-Si.[6] The advantages of this method are:(1) The size of the nc-Si can be effectively controlled by predesigning the thickness of the a-Si:H sublayer; (2)fabricated nc-Si is embedded in an a-SiN_x:H matrix so that its surface has been passivated. Intensive, visible and stable photoluminescence (PL)[7] and electroluminescence (EL)[8] at the room temperature have been observed from the nc-Si prepared by this method.

Recently more efforts are put on the electrical properties of nanometer materials for the application in nano-electronics. Since single-layer nc-Si structures may be used as key elements in these devices, the fabrication of the single-layered and size-controlled nc-Si has drawn much attention these years. In Ref.[9], Fujita reported visible EL could be obtained in single-layer nc-Si dots prepared by thermal annealing of the a-Si. But the high temperature treatment is not a good way for device processing. On the other hand, the thermal annealing technique cannot produce a patterned crystallization, which is required for device fabrication. However, laser annealing can produce patterned crystallization by placing the mask on the surface of the sample.

In this paper, we combine the principle of constrained crystallization with the technique of laser interference crystallization to obtain the ultra-thin single-layer, size-controlled and patterned nc-Si dots within the sandwiched structure (a-SiN_x:H/a-Si:H/a-SiN_x:H) films. The fabrication and characterization

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of the samples are presented and discussed.

Ⅱ. EXPERIMENTAL

The sandwiched structure a-SiN_x:H(50nm)/a-Si:H(10nm)/a-SiN_x:H(50nm) films were deposited on the substrates of fused quartz by the 13.56 MHz r.f. plasma-enhanced chemical vapor deposition (PECVD) technique. During the deposition, the gases of SiH_4(8sccm)/NH_3(40sccm) and SiH_4(8sccm) were diuted by Ar_2 for the fabrication of a-SiN_x:H and a-Si:H respectively; the temperature of the substrate was 250°C. The deposition rate was about 5.4nm/min.

The samples were irradiated by KrF excimer laser with wavelength of 248 nm and pulse duration of 30ns. We placed the sample behind the silica phase mask grating with surface-relief structure of 2μm periodicity and 260nm depth with a certain distance to create the patterned crystallization in the lateral. The laser beam, which passed at normal incidence through the mask, was phase modulated spatially, and diffracted to form a high-contrast intensity interference pattern with a periodicity of 2μm on the surface of the sample.

The crystallinity and microstructure of the films after laser annealing were verified by Raman scattering spectroscopy, planar and cross-section transmission electron microscopy (TEM) and electron diffraction(ED).

Ⅲ. RESULTS AND DISCUSSIONS

The fabrication of ultra-thin and single-layered nc-Si materials is very difficult because the energy density of the laser is very critical in crystallization. For preparing the patterned crystallization in samples, we first studied the dependence of energy density on the laser crystallization of the sandwiched structure a-SiN_x:H(50nm)/a-Si:H(10nm)/a-SiN_x:H(50nm) samples without mask covered on it. We found that at a higher laser energy density, the sandwiched structures and the irradiated surface region were damaged; at a lower laser energy density, Si nanocrystallines cannot be formed in a-Si layer. The nc-Si dots embedded in a SiN_x:H layers can be obtained by using moderate laser energy density. We found that the energy density between 75 and 85 mJ/cm^2 is suitable for the crystallization of the above sample by trying a series of experiments. Figure 1 shows the Raman scattering spectroscopy of the sample after laser irradiation at the energy density of 80 mJ/cm^2. The band at ~480cm^{-1} is connected with some amorphous phase, while the peak at 518cm^{-1} is due to scattering by optical photons in nc-Si. The peak does not appear in the as-deposited sample. The average size of nc-Si in this sample is estimated to be 9.6nm according to the photon confinement model.[10] The ED pattern in Fig.2 again confirms that the layer of a-Si has been crystallized. The planar TEM image in Fig.2 indicates that the lateral sizes of nearly uniform-sized nc-Si dots are about 10±2nm, almost the same as the designed thickness of the a-Si in the longitudinal direction.

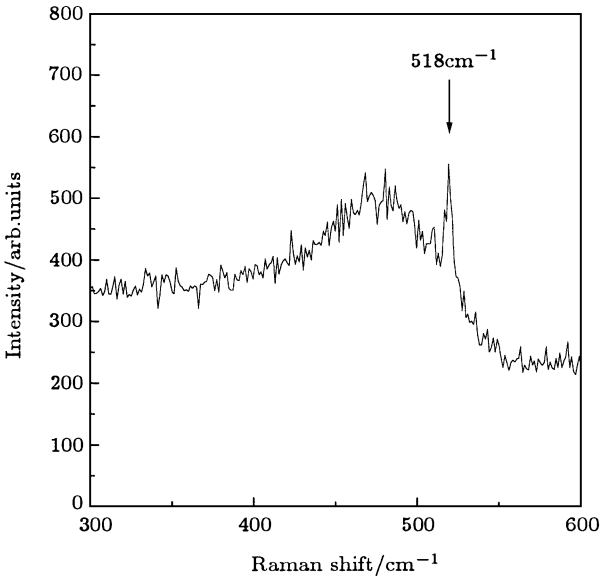


Fig.1. The Raman spectrum of the crystallized sample of sandwiched structure a-SiN_x:H(50nm)/a-Si:H(10nm)/a-SiN_x:H(50nm)prepared by laser crystallization at the energy density of 80.0 mJ/cm^2.

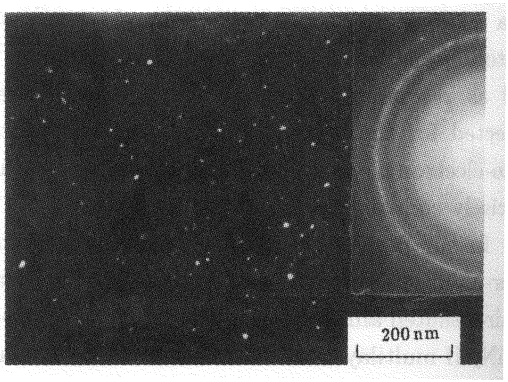


Fig.2. The planar TEM photograph (dark field) and ED pattern of the same sample as in Fig.1.

To obtain the patterned crystallization in the as-deposited samples, we introduce a phase-shifting mask during the laser crystallization. The laser energy distribution is modified periodically in the manner as we

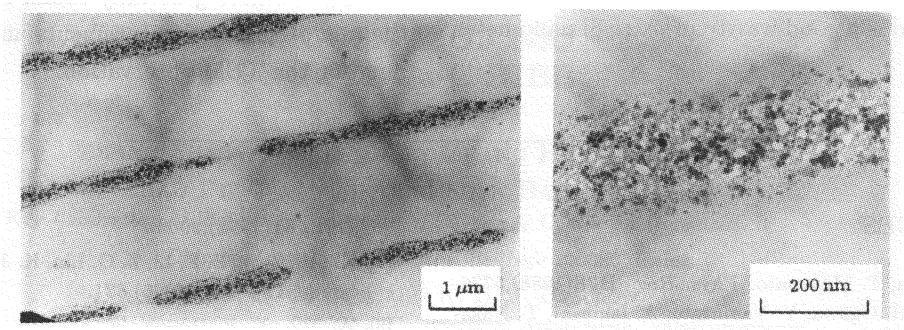


Fig.3. (a) The planar TEM photograph of the patterned crystallized sandwiched structure a-SiN$_x$:H(50nm)/a-Si:H(10nm)/a-SiN$_x$:H(50nm), prepared by laser interference crystallization at the energy density of 39.0 mJ/cm^2.(b) The planar TEM photograph of the magnified part of one stripe shown in Fig.3(a).

calculated before.[11] The energy density required for the patterned crystallization is reduced compared with that of the above samples.

Figure.3(a) is the planar TEM photograph of the sample with a sandwiched structure irradiated by the laser with energy density of 39mJ/cm^2. The crystallized areas with a width of ∼200 nm and a periodicity of 2μm correspond to the laser interference crystallized regions. In optical micrographs, these stripes could be seen more clearly due to the difference in the optical absorption of the amorphous and crystalline phases. And the magnified part of the one stripe shown in Fig.3(b) indicates that the interfaces between the crystallized and the amorphous zones are abrupt due to the well-defined intensity threshold for laser crystallization of a-Si film and the sizes of nc-Si are nearly uniform. As seen in the cross-section TEM photograph of Fig.4, the Si crystallites are closely arranged one by one in the stripe, with their grain sizes being roughly equal to the layer thickness. The interfaces between Si layer and SiN$_x$ layers are still flat after laser irradiation.

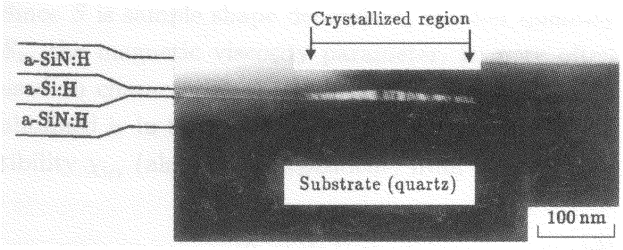


Fig.4. The cross-section TEM photograph of the sample shown in Fig.3.

We have successfully controlled the size of nc-Si dot in the longitudinal direction and patterned the crystallites in the lateral direction during the laser interference crystallization of the sandwiched structure. The above results can be explained by the principle of constrained crystallization. The crystallization occurs only within a-Si:H layer because in case of using the KrF laser (248nm) the optical absorption coefficient of a-Si is about two orders larger than that of a-SiN$_x$:H, while a-SiN$_x$:H has a much higher thermal stability than a-Si:H. Therefore, the a-Si:H layers are crystallized under the constraint of neighboring stable a-SiN$_x$:H layers. The longitudinal size of nc-Si is determined by the predesigned thickness of a-Si layer. Because in the case of sphericity the surface is minimal when the volume is constant, the shape of the nc-Si dots is spherical according to the principle of minimum surface energy.

In order to obtain a deeper understainding of the constrained crystallization, we use a sample of single-layer a-Si:H that has no a-SiN$_x$:H covered on either side to be irradiated by laser, but the distribution of the sizes of nc-Si dots is much broader than that in the film of the sandwiched structure. This is the direct evidence that the effect of barrier layer a-SiN$_x$ is very important in the constrained crystallization in order to get a uniform size distribution of nc-Si.

IV.CONCLUSION

The single-layered, uniform-sized nc-Si dots can be obtained during laser interference crystallization of the sandwiched structure under the condition of proper energy density. The size of nc-Si dots is determined by the thickness of the a-Si layer in the longitudinal direction and the crystallized areas can be patterned in the lateral direction. The results show the

present method is a good way to prepare Si nanometer devices.

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