

Visible Photoluminescence from Hydrogenated Amorphous Silicon Thin Films Deposited on Silicon Substrates by Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition

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ECR-PECVD로 증착한 a-Si : H/Si로 부터의 가시 Photoluminescence

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초 록 SiH₄를 반응물질로 사용하여 electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD)로 실리콘 기판위에 증착한 수소화 비정질 실리콘 (a-Si : H) 으로부터 가시 photoluminescence (PL)가 관찰되었다. a-Si : H/Si로 부터의 PL은 다공질실리콘으로부터의 PL과 유사하였다. 급속열처리에 의해 500°C에서 2분간 산소분위기에서 어닐링된 시편의 수소함량은 1~2%로 줄어들었고 시편은 가시 PL을 보여주지 않았는데 이는 a-Si : H의 PL 과정에서 수소가 중요한 역할을 한다는 것을 뜻한다. 증착된 a-Si : H의 두께가 증가함에 따라 PL의 세기는 감소하였다. SiH₄를 사용하여 ECR-PECVD에 의해 Si상에 증착된 a-Si : H로부터의 가시 PL은 Si과 증착된 a-Si : H막 사이에 증착이 이루어지는 동안에 형성된 수소화실리콘으로부터 나오는 것으로 추론된다.

Abstract Visible photoluminescence(PL) was observed from hydrogenated amorphous silicon deposited on silicon(a-Si : H/Si) using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) with silane (SiH₄) gas as the reactant source. The PL spectra from a-Si : H/Si were very similar to those from porous silicon. Hydrogen contents of samples annealed under oxygen atmosphere for 2minutes at 500°C by rapid thermal annealing were reduced to 1~2%, and the samples did not show visible PL, indicating that hydrogen has a very important role in the PL process of a-Si : H/Si. As the thickness of deposited a-Si : H film increased, PL intensity decreased. The visible PL from a-Si : H deposited on Si by ECR-PECVD with SiH₄ is suggested to be from silicon hydrides formed at the interface between the Si substrate and the deposited a-Si : H film during the deposition.

I. Introduction

Recently, there has been a lot of research on silicon-based light emitting materials, which can be incorporated into the well-established silicon integrated circuits to form silicon-based optoelectronic integrated circuits. Porous silicon was observed to emit a strong photoluminescence at room temperature.¹⁾ The origin of the luminescence from porous silicon is not fully understood, and there are several suggestions for the origin of the photoluminescence from porous silicon. Quantum size effect in the pillars of porous silicon was suggested by Canham¹⁾ to be the origin of the photoluminescence. Qin and Jia proposed quantum confinement/luminescent model, in which electrons are excited within nanoscale silicon and then deexcited via luminescent centers in SiO₂ layers.²⁾ Proke *et al.*³⁾ and Tsai *et al.*⁴⁾ reported that

photoluminescence from porous silicon is due to silicon hydrides, SiH_x, which form at the interface between the air and porous silicon during the anodizing process in HF solution.

Even with the intense luminescence, porous silicon is difficult to be used in integrated optoelectronic circuits due to the anodizing step to make the silicon surface porous. It is very desirable to make silicon-based light emitting materials by deposition, which can be easily added to standard silicon integrated circuit processes.

In this paper, we report that visible photoluminescence(PL) was observed from hydrogenated amorphous silicon (a-Si : H) thin films deposited on silicon substrates using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) with silane as the reactant gas source.

II. Experiments

Si(100) substrates were cleaned with organic solvents and rinsed with deionized water (DI water) before they were cleaned in a mixture solution of DI water, H₂O₂ (30%), and NH₄OH (29%) with the volume ratio of 5 : 1 : 1 at 40°C for 10 minutes. After being rinsed with cold DI water, substrates were treated with H₂O : HF = 10 : 1 solution to remove the native oxide on them. Substrates were rinsed again, dried thoroughly in N₂ blow and then loaded into the deposition chamber of the ECR-PECVD system. Detailed description of the ECR-PECVD system is in Ref. 5. Briefly, the plasma chamber is 270mm in diameter and 300mm in height. The deposition chamber is 420mm in diameter and 400mm in height. The pumping system consists of a rotary pump and a turbomolecular pump. The base pressure of 10^{-6} torr was achieved by the turbomolecular pump before each deposition. The working pressure is high order of 10^{-4} torr. The microwave power is introduced into the plasma chamber through a rectangular waveguide and a quartz window. The magnetic coil is arranged around the periphery of the plasma chamber and the magnetic field is applied to it for ECR plasma formation. Ar (5sccm) gas is introduced into the plasma chamber and SiH₄ (40sccm) gas is introduced into the deposition chamber as a source gas. The plasma stream is introduced into the deposition chamber through the limiting ring. The thicknesses of deposited a-Si : H films were measured by a surface profilometer (α -step) and confirmed by spectroscopic ellipsometer. Spectroscopic ellipsometry (SE) measurement in the energy region 1.5–4.0eV was performed on a-Si : H films at room temperature using UV-visible phase-modulated ellipsometry (UVISEL, Jobin Yvon). Fourier-transform infrared (FTIR) spectroscopy measurement was used to investigate the Si-H bonding. Photoluminescence (PL) spectra from a-Si : H films were taken at room temperature. PL excitation was provided by the 364nm line of an Ar ion laser with the power of 400mW.

III. Results and discussion

Figure 1 shows the PL spectra from a-Si : H films deposited on Si(100) substrates. Aluminum susceptor and stainless susceptor were used for the deposition of samples (a) and (b), respectively. Although samples (a) and (b) were deposited without any thermal heating, substrate temperatures of (a) and (b) were increased to 80°C and 140°C, respectively, by plasma heating. Since aluminum has higher thermal conductivity than stainless steel, the temperature of the sample (b) was higher than that of sample (a). Aluminum

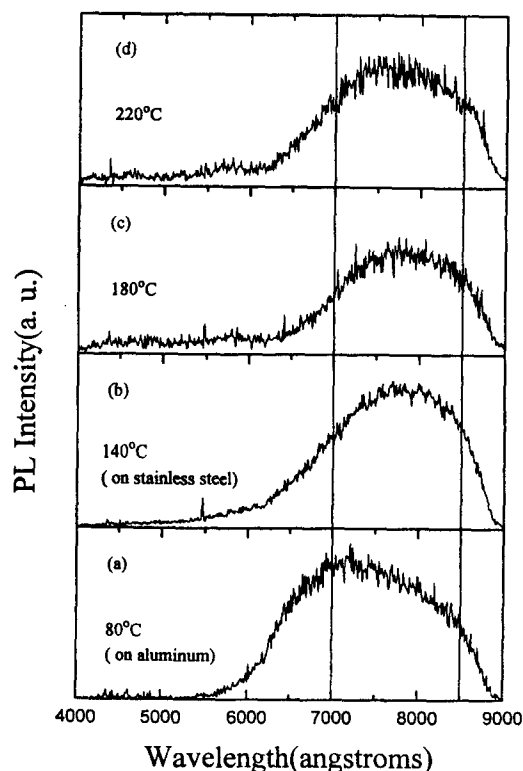


Fig. 1. Room-temperature photoluminescence spectra of a-Si : H films deposited on Si. Excitation was provided by the 364nm line of an Ar ion laser with the power of 400mW. See the text for specifications of (a) to (d).

susceptor was used for both sample (c) and sample (d). Deposition temperatures 180°C and 240°C were maintained for sample (c) and sample (d), respectively, by thermal and plasma heating. All the PL spectra in figure 1 contains part of the visible range of the optical spectrum, and red luminescences from the samples were observed by naked eyes. These spectra are very similar to previously reported ones for porous silicon.^{3,4)} Figure 2 shows the variation of the hydrogen contents (C_H) of a-Si : H films, samples (a), (b), (c) and (d) in figure 1, with the deposition temperatures. C_H decreased as the deposition temperature increased. The inset of figure 2 shows the FTIR spectrum of sample (a) in figure 1. Four absorption bands, near 2100, 890, 845, and 640 cm^{-1} , were observed and assigned to the stretching, bending, wagging, and rocking modes, respectively, of SiH₂ groups. In (a) and (b), as the deposition temperature increased and C_H decreased, the PL showed a clear red-shift as shown in Refs. 3 and 4, while for (b), (c) and (d) the red-shift with the deposition temperature is not so obvious. In Refs. 3 and 4, the red-shifts of PL spectra from porous silicon with increasing annealing temperature were attributed to the desorption of silicon hydrides from the porous silicon surface. All the samples were annealed at 500°C for 2minutes under oxygen atmosphere by rapid thermal

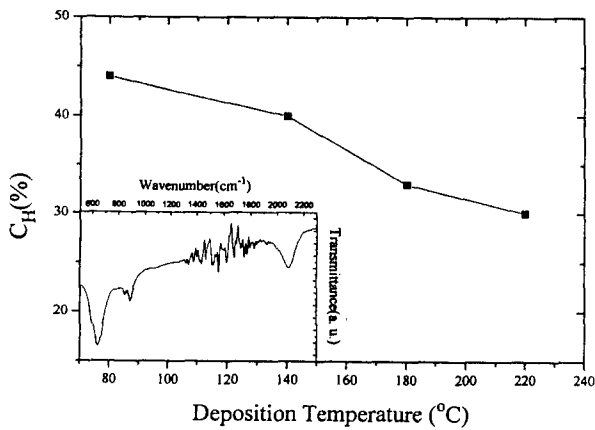


Fig. 2. Hydrogen content (C_H) as a function of the deposition temperature for a-Si : H film deposited on Si. The inset is the FTIR spectrum of sample (a) in figure 1.

annealing. After the rapid thermal process, hydrogen contents of all the samples were reduced to 1~2%, and the samples did not show visible photoluminescence any more. This indicates that the visible PL from a-Si : H film is strongly related to hydrogen in the film. This result is the same as those reported in Refs. 3 and 4, in which intensity of PL from porous Si dropped rapidly as the SiH_x group disappeared.

Figure 3 shows the PL spectra change with the thickness of the deposited a-Si : H film. The deposition condition of the film is the same as that of sample (a) in figure 1. The thickness of the film was changed by varying the deposition time. As the thickness of the film increased, the PL intensity decreased. The 281nm thick film almost did not show visible photoluminescence. The result shown in figure 3 indicates that the PL from a-Si : H deposited on Si is not from a-Si : H itself. If the luminescence had been from the a-Si : H, the luminescence would have increased and then saturated as the thickness of the deposited a-Si : H film increased. Since neither Si nor a-Si : H showed any visible PL in our experiments, PL from a-Si : H on Si can be suggested to be from the interface between the substrate and the deposited a-Si : H film. In Refs. 3 and 4, the SiH_x groups, which were formed at the interface between the air and the crystalline silicon in pillars of the porous silicon during anodizing process in HF solution, were found as the origin of the visible PL from porous silicon. In our case, it can be suggested that SiH_x groups were formed at the interface between the crystalline Si substrate and the deposited a-Si : H film during the deposition and are the origin of the visible PL from a-Si : H deposited on a Si substrate. The disappearance of visible PL from a-Si : H/Si after annealing at 500°C can be attributed to the desorption of silicon hydrides from the interface. The decrease and disappearance of PL intensity due to the desorption of SiH_x groups from

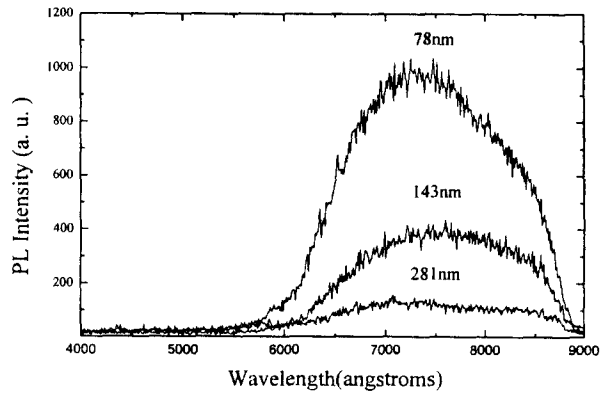


Fig. 3. PL spectra for a-Si : H films deposited on Si substrates. The thicknesses of the films were 78nm, 143nm, and 281nm.

the air-porous silicon interface with increasing annealing temperature was also reported in Refs. 3 and 4.

IV. Conclusions

In summary, visible photoluminescence was observed in a-Si : H film deposited on Si by electron cyclotron resonance plasma enhanced chemical vapor deposition using SiH₄ as the reactant gas source. These spectra were very similar to those from porous silicon. Samples annealed in two minutes at 500°C by rapid thermal annealing showed hydrogen content of 1~2%, and did not show visible photoluminescence. Thicker films did not show PL, indicating that PL is not from a-Si : H itself, but from the interfaces between the substrates and the deposited films. The origin of the visible luminescence from the a-Si : H film deposited on Si is suggested to be silicon hydrides formed at the interface between the crystalline silicon and the deposited a-Si : H film during the deposition.

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