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Visible Photoluminescence of Highly Photoconductive Hydrogenated Amorphous Silicon Film

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A highly photoconductive hydrogenated amorphous silicon (a-Si:H) film showing visible photoluminescence (PL) has been obtained by a plasma CVD method using SiH₄ highly diluted with He. The PL increases rapidly and blueshifts consistently with the increase of the SiH₂ and (SiH₂)_n configurations in the a-Si:H film. The a-Si:H film with wide band gap (>2.0 eV) exhibits a visible PL at room temperature and a photoconductivity to dark conductivity ratio of over 10^6 under AM-1 light of 100 mW/cm^2 . By the observation using transmission electron microscope technique, it is found that the film consists of uniform amorphous structure.

1. INTRODUCTION

It is well known that hydrogenated amorphous silicon (a-Si:H) film has high photoconductivity for visible light. However, a-Si:H has been hardly expected for visible light emission because the band gap of a-Si:H is ordinarily small (1.7-1.8 eV) and it is difficult to fabricate a-Si:H film with wide band gap (>2.0 eV) by general glow-discharge method using silane (SiH_4) .

Recently, the authors have obtained a highly photoconductive a-Si1-xCx:H film with wide band gap (>2.0 eV) by rf glow discharge of source gases, SiH4 and C2H2, highly diluted with He.¹⁻⁴⁾ We have also tried the application of the He-dilution method to a-Si:H deposition. To the authors' knowledge, we have first succeeded in depositing highly photoconductive a-Si:H films with wide band gap (>2.0 eV) by the SiH₄ plasma highly diluted with He, and we have observed visible photoluminescence (PL) from these films at room temperature. In this work, the correlation between the luminescence and the film structure has been discussed on the basis of the experimental results.

2. EXPERIMENTS

The a-Si:H films were prepared by capacitance-coupled rf (13.56 MHz) glow discharge of SiH₄, diluted with He. Deposition conditions are summarized in Table 1. Total gas flow rate (F_t) of 170 sccm was fixed. To investigate the He-dilution effect of a-Si:H, the SiH₄ concentration, $R(SiH_4)=SiH_4/F_t$, was changed from 250 ppm to 2 % in volume. Undoped a-Si:H films $\sim 1 \ \mu$ m thick were deposited on fused silica for the measurements of the optical and electrical properties, on frosted glass (Corning #7059) for PL spectrum measurements and on FZ crystal silicon for infrared (IR) spectrum measurements.

To investigate the annealing effect, the sample grown with $R(SiH_4)=500$ ppm was annealed at temperatures in the range 250 - 450°C for 30 min in a vacuum below 1×10^{-4} Pa.

The PL spectrum was measured at room temperature (298 K) and at liquid nitrogen temperature (80 K) using an Ar-ion laser light of 11.7 mW at 488 nm for excitation.

Table 1 . Deposition conditions.

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Flow rate	
SiH4	0.56-3.4 sccm
He	166.6-169.5 sccm
RF power density	80 mW/cm ² (13.56 MHz)
Pressure	1.1x10 ² Pa
Substrate temp.	100°C
Substrate	fused silica, #7059, c-Si

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Figure 1 shows PL spectra at 80 K from the a-Si:H films prepared with various $R(SiH_4)$ values between 250 ppm and 2 %. Below 0.5 % of $R(SiH_4)$, the PL at 900 nm increases noticeably and blueshifts consistently to 750 nm. At room temperature, red PL in the films below 0.1% of $R(SiH_4)$ was also observed by the naked eye.

Figure 2 shows the optical band gap

determined by using the h ν vs. $(\alpha h\nu)^{1/2}$ plot as a function of R(SiH₄). The optical band gap increased sharply with He-dilution of SiH₄, below 0.5 % of R(SiH₄). This result coincides with the behavior of the PL peak shown in Fig. 1.

IR absorption spectra for the a-Si:H films prepared with various $R(SiH_4)$ are shown in Fig. 3. Decreasing $R(SiH_4)$ below 0.5 %, the 840 cm⁻¹ and 890 cm⁻¹ peaks which are assigned to the $(SiH_2)_n$ bending mode and the SiH_2 and $(SiH_2)_n$ (n=2,3,...) bending modes, respectively, show a marked increase. The 2000cm⁻¹ peak assigned to the SiH stretching mode is shifted toward higher wave number, 2090 cm⁻¹ assigned to the SiH₂ and $(SiH_2)_n$ stretching modes, with He-dilution. The blueshift of the PL peak and the expansion of the band gap with the decrease of $R(SiH_4)$ are attributed to



Fig. 1 PL spectra at 80 K for samples under various SiH4 concentrations, R(SiH4).



Fig. 2 Optical band gap of samples as a function of the SiH4 concentration, R(SiH4).

the increase of the SiH_2 and $(\rm SiH_2)_n$ configurations in the film.

Figure 4 shows a series of PL spectra of the sample $[R(SiH_4)=500 \text{ ppm}]$ for various annealing temperatures between 250 and 400°C. As the annealing temperature increases, the PL at 800 nm decreases rapidly and shifts toward longer wavelength.

Figure 5 shows absorption coefficients of various IR peaks in the sample $[R(SiH_4)=500 \text{ ppm}]$ as a function of the annealing temperature. The absorption coefficients of 840 cm⁻¹







Fig. 4 PL spectra at 80 K of the sample grown with R(SiH₄)=500 ppm for various annealing temperatures.

 $[(SiH_2)_n]$ and 2090 cm⁻¹ $[SiH_2$ and $(SiH_2)_n]$ decrease rapidly in comparison with that of 2000 cm⁻¹ (SiH). From the results in Figs. 4 and 5, it is confirmed that the visible luminescence is attributed to the SiH₂ and (SiH₂)_n configurations.

A section of the film showing visible luminescence was observed with transmission electron microscope (TEM). Figure 6 shows TEM image of the as-deposited sample $[R(SiH_4)=500$ ppm]. We have found that the film consists of uniform amorphous structure and includes no microcrystallites, as shown in porous silicon.⁵⁾ Therefore, the visible luminescence is emitted from the bulk of the a-Si:H film.

Figure 7 shows the dark- (σ d) and photoconductivities (σ _{ph}) of the as-deposited films as a function of R(SiH₄). Under illumination of AM-1 light at 100 mW/cm², σ _{ph}



Fig. 5 Absorption coefficients at various IR peaks of the sample grown with R(SiH₄)= 500 ppm as a function of the annealing temperature.



Fig. 6 Cross-sectional TEM image of the film grown with R(SiH4)=500 ppm.



Fig. 7 Dark- and photoconductivities of the a-Si:H films as a function of the SiH₄ concentration, R(SiH₄).

was measured. As shown in Fig.7, the samples in the region below 0.1 % of R(SiH₄) exhibit high photoconductivities and large photogain ($\sigma_{\rm ph}/\sigma_{\rm d}$), over 10⁵. It means that these films have a potential of an application to not only a light emitting device but also a photodetector.

4. CONCLUSION

We have described the structure and the luminescence properties of wide-gap (>2.0 eV) a-Si:H films prepared by a He-dilution plasma CVD method using SiH₄. The a-Si:H films show both high photoconductivity and visible luminescence. These new a-Si:H films will provide an optical device with characteristics of both light emission and photosensitivity and OEIC with a large area, which will be useful in the implementation of optical image processing and optical neurocomputing systems.

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