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 SiH₄ 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 10⁴ under AM-1 light of 100 mW/cm². 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 (SiH₄). Recently, the authors have obtained a highly photoconductive a-Si:C,H film with wide band gap (>2.0 eV) by rf glow discharge of source gases, SiH₄ and CH₄, highly diluted with He. 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 (Fₜ) of 170 sccm was fixed. To investigate the He-dilution effect of a-Si:H, the SiH₄ concentration, R(SiH₄)=SiH₄/Fₜ, was changed from 250 ppm to 2 % in volume. Un-doped a-Si:H films ~1 µm 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(SiH₄)=500 ppm was annealed at temperatures in the range 250 - 450°C for 30 min in a vacuum below 1x10⁻⁷ 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.

| Flow rate | SiH₄ | 0.56-3.4 sccm | He | 166.6-169.5 sccm |
| RF power density | 80 mW/cm² (13.56 MHz) | Pressure | 1x10⁻⁷ 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(SiH₄) values between 250 ppm and 2 %. Below 0.5 % of R(SiH₄), 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(SiH₄) was also observed by the naked eye.

Figure 2 shows the optical band gap...
determined by using the $h\nu$ vs. $(a h\nu)^{1/2}$ plot as a function of $R(SiH_4)$. The optical band gap increased sharply with He-dilution of $SiH_4$ below 0.5% of $R(SiH_4)$. 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 $(SiH_3)_b$ bending mode and the $SiH_4$ 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 $SiH_2$ 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 the increase of the $SiH_2$ and $(SiH_2)_n$ configurations in the film.

Figure 4 shows a series of PL spectra of the sample [$R(SiH_4)$=500 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 ppm] as a function of the annealing temperature. The absorption coefficients of 840 cm$^{-1}$...
[(SiH₂)ₙ] and 2000 cm⁻¹ [SiH₃] decrease rapidly in comparison with that of 2000 cm⁻¹ [SiH₄]. From the results in Figs. 4 and 5, it is confirmed that the visible luminescence is attributed to the SiH₂ and (SiH₃)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(SiH₄)=500 ppm]. We have found that the film consists of uniform amorphous structure and include no microcrystallites, as shown in porous silicon. Therefore, the visible luminescence is emitted from the bulk of the a-Si:H film.

Figure 7 shows the dark- (σᵩ) and photoconductivities (σ₊) of the as-deposited films as a function of R(SiH₄). Under illumination of AM-1 light at 100 μW/cm², σ₊ was measured. As shown in Fig. 7, the samples in the region below 0.1 % of R(SiH₄) exhibit high photoconductivities and large photogain (σ₊/σ₀), over 10⁴. 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.

REFERENCES