Journal of Optoelectronics and Advanced Materials Vol. 7, No. 1, February 2005, p. 499 - 502

PHOTOLUMINESCENCE OF HYDROGENATED AMORPHOUS SILICON SUBOXIDES

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The photoluminescence properties of a hydrogenated amorphous silicon suboxide film with 26.2 at.% oxygen has been studied in the as-deposited state and after post annealing procedures at elevated temperatures. Two typical silicon suboxide PL bands, at 2.1 eV and at 1.85 eV, were observed. From temperature dependent measurements, it was demonstrated that the intensity of the 2.1 eV PL band is thermally activated, with an activation energy of 0.49 eV. The 2.1eV band is attributed to oxygen related defect transitions, whereas the 1.85 eV band may be attributed to localised to localised state transitions.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Silicon suboxides, a-SiO_x:H, Photoluminescence, CPM

1. Introduction

Hydrogenated amorphous silicon suboxides (a-SiO_x:H; x<2), among other wide band-gap hydrogenated amorphous silicon based alloys, are very attractive, with visible room temperature photoluminescence (PL) properties and a higher photosensitivity than other materials with similar optical gaps [1].

Three main PL features, at the photon energies of about 2.9 eV, 2.1 eV and 1.7 eV are observed for the a-SiO_x:H alloys [2]. In order to explain these bands, several models have been suggested. The most popular ones are luminescence from nanometer sized amorphous silicon rich regions separated throughout the SiO_x matrix [3], non-bridging oxygen hole centers (NBOH; ≡Si-$O^{\bullet}$) [4], and triplet to ground state transitions of neutral oxygen vacancy defects, (≡Si-Si≡) [5]. Radiative recombination between band tails can also be observed between 1.7 eV-1.9 eV [6]. On the other hand, band to band transitions are expected to be less probable at room temperature, since the radiative transition lifetime is much longer than the non-radiative lifetime in a-Si:H [6]. The effect of post annealing treatment subsequent to the deposition of a-SiO_x:H films on the PL properties has also been studied, to verify the validity of the proposed models [2].

In this work, 2.1 eV and 1.7-1.9 eV PL bands of an a-SiO_x:H film ([O]=26.2 at.%) is investigated in as deposited state and after post annealing at 400 °C, 600 °C and 800 °C. Two room temperature PL bands at 2.1 eV and at 1.85 eV are observed and variation of peak PL intensity with measurement temperature is examined in detail for as deposited and annealed films. Similar PL bands has also been observed for a-SiO_x:H films with different oxygen concentrations [1] and results will be presented elsewhere.

2. Experimental details

Hydrogenated amorphous silicon oxygen alloy thin films were deposited on crystalline silicon substrates by RF-plasma decomposition of a CO_2+SiH_4 gas mixture at 20MHz, with an RF

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power density of 69 mW/cm^2, a total chamber pressure of 200 mTorr and a substrate temperature of 300 °C. Oxygen incorporation was realised by varying the ratio of the partial pressure of CO_2 to the total gas pressure. FTIR measurements were performed to estimate the oxygen concentration [O] in the film. This can be estimated by integrating the absorption feature around 1000 cm^{-1}, that is due to Si-O-Si asymmetric band stretching vibrations [7], giving a calculated value of 26.2 at.%.

The constant photocurrent method (CPM) (details in [1]) and optical transmission measurements at room temperature were used to determine the absorption spectrum. The Tauc gap of the as-deposited film was estimated to be 2.18 eV. Three pieces of the samples were annealed in vacuum at temperatures of 400, 600 and 800 °C for 30 min. in order to examine the effect on PL feature. The Tauc gaps were found to be reduced to 1.97, 1.74 and 1.67 eV, respectively.

An ARS-202N model closed cycle He cryostat was used, with a temperature range 20 to 420 K. For PL measurements, the 488nm mode of a Melles Griot Ar^+ ion laser as the excitation source and Jobin-Yvon Triax 550 monochoromator were employed. Photon detection was made using a photomultiplier tube. A series of experiments was performed in the temperature range 400 to 50 K, in 50 K steps, and also at 20 K. A 900 °C vacuum furnace was designed for the post-annealing procedures. After taking the PL spectra, some smoothing procedures were made to reduce the electronic noise. Then, for every observed PL band, Gaussian fittings were used to obtain the physical parameters.

3. Results

The optical absorption and PL spectra of an as-deposited film, measured at 300 K, are plotted versus photon energy in Fig. 1. The position of the Tauc gap is also indicated. The centre of the PL peak is located at 2.1 eV. The energy position of this PL feature was also recorded in our other suboxide samples with different oxygen concentrations. PL experiments of the as-deposited sample were performed in the temperature range 400 to 20 K. The results are presented in Fig. 2. The intensity of the 2.1 eV PL peak was higher at 350 K than at 400 K. As the temperature decreased, the PL intensity also decreased, and the peak value of the spectra shifted slightly from 2.1 eV to 2.2 eV at very low temperatures. At temperatures below 150 K, another peak that is obscured at higher temperatures appeared at about 1.85eV. A further decrease in the temperature caused the intensity of the 1.85eV band to increase. At 20K, this band showed the highest intensity, and almost no signal at 2.1eV was detected. The half-widths of the 2.1 eV band were unchanged, at about 0.34eV, for almost all temperatures. However the half-width of the 1.85 eV band slightly decreased with increasing temperature, from 0.37 eV at 20 K to 0.30 eV at 200 K.

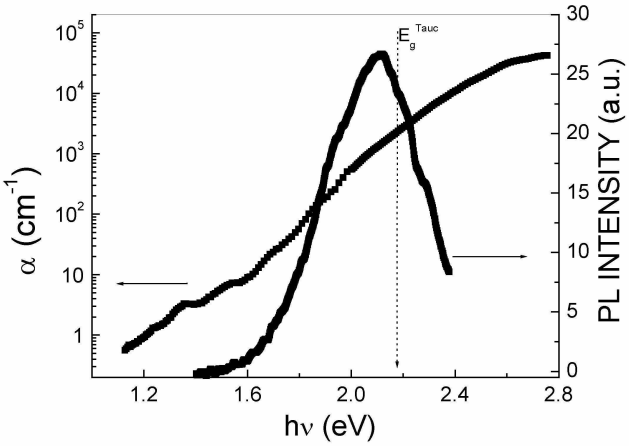

Fig. 1. Room temperature absorption and PL spectra of an as-deposited a-SiO_x:H sample, with [O]=26.2 at.%.

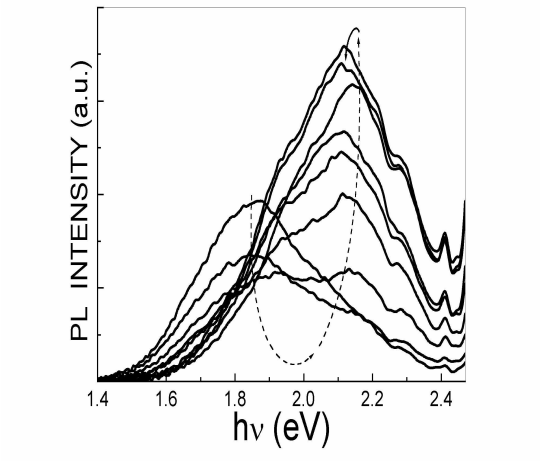

Fig. 2. Temperature dependent PL spectra of as-deposited a-SiO_x:H. The dashed and solid arrowed lines show increasing temperature from 20 to 400K. (the PL intensity at 400K was lower than at 350K, as indicated by the solid line.)

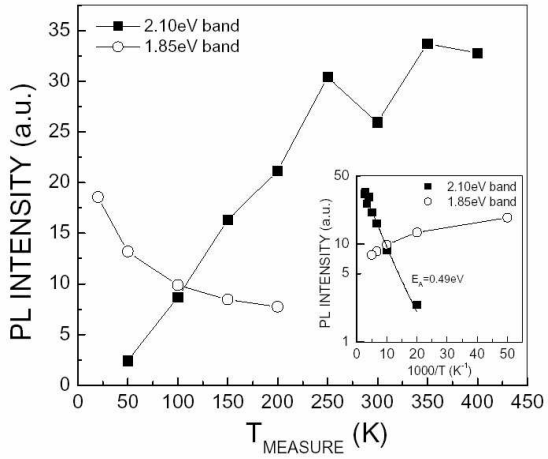

Fig. 3. PL peak intensities of the 2.1eV and 1.85eV bands of as-deposited a-SiO_x:H, with respect to the measurement temperature. In the inset, the same data are plotted as a function of 1000/T.

The PL intensity (in arbitrary units) of the 2.1 and 1.85 eV bands of an as-deposited sample with respect to temperature is given in Fig. 3. For elevated temperatures, the 2.1 eV band intensity increased monotonically. The intensity of the 1.85 eV band was reduced by more than a factor of two as the temperature decreased. Above 200 K, the 1.85 eV band could not be measured, since it was obscured under the growing 2.1 eV band. The inset in Fig. 3 exhibits the PL intensity versus 1000/T. The 2.1 eV band intensity was found to be activated, with an energy of 0.49 eV.

Three pieces of the same sample were subjected to post annealing at 400, 600 and 800 °C. The PL of these films was measured as a function of temperature. The 1.85 eV band was not observed for these samples. In Fig. 4, the deduced peak intensities are plotted as a function of temperature. Subsequent to the post annealing procedure at elevated temperatures, the 2.1 eV PL intensity decreased drastically. Interestingly, below 75 K the PL intensity of the sample annealed

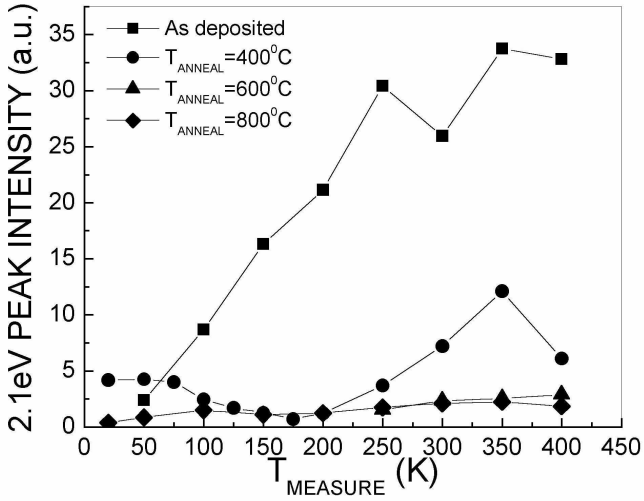

Fig. 4. Temperature dependence of PL spectra of post-annealed and as-deposited a-SiO_x:H samples.

at 400 °C increased as the temperature decreased. Above 200 K, the PL intensity of this sample increased to more than twice its value at 350 K, and decreased back again at 400 K. The peak values of the PL spectra for the samples annealed at 600 and 800 °C were less than 2.1 eV. However, they shifted to 2.1 eV as the temperature increased.

4. Discussion

Since the 2.1 eV PL peak was observed to be independent of the oxygen concentration in the films, a different mechanism that is inactive in a-Si:H is responsible for the observed PL in silicon suboxides. Post annealing of the sample at elevated temperatures led to a drastic decrease in the PL intensity of the 2.1 eV band. This result is in agreement with a previous work [2], while an opposite result has also been observed within a certain oxygen concentration range [8], in a limited number of studies in the literature. Upon annealing, hydrogen effusion from the films occurs [2]. Moreover, the observed activation-like increase in the 2.1 eV band of the PL intensity seems to favour defect like transitions as being responsible for this peak, and also the importance of H atoms. Thus, our data support two previously suggested models; a non-bridging oxygen hole centre (NBOH; ≡Si-O$^{\bullet}$) [4], and the triplet to ground state transition of a neutral oxygen vacancy defect (≡Si-Si≡) [5], as would be responsible for the observed 2.1 eV PL band. Moreover, the observed temperature dependent increase of the 2.1 eV photoluminescence band with 0.49eV activation energy could be related to the enhanced surface diffusion of carriers towards radiative recombination centres.

Temperature quenching of the PL intensity of the 1.85 eV band is in agreement with the model of temperature quenching of localised to localised state transitions in a-Si:H [6]. On the other hand, the fixed energy position of this peak, and its disappearance after post annealing, seems to be against it. Also, the similar increase of the 2.1 eV PL intensity, at very low temperatures, for the film annealed at 400 ^{o}C, is not easy to link to such a transition, given the band gap of this film.

5. Conclusions

The 2.1 eV and 1.7-1.9 eV PL bands of a representative hydrogenated amorphous silicon suboxide film have been investigated using temperature dependent PL measurements. The observed activation-like increase in the 2.1eV PL intensity, with an activation energy of 0.49 eV, and the reduction of the PL signal upon post annealing treatment of the films suggest that an oxygen related defect transition could be responsible for this feature. On the other hand, the 1.85 eV PL peak may be attributed to localised to localised state transitions. More work is under way to investigate the PL properties of such a-SiO_x:H films.

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