Journal of Optoelectronics and Advanced Materials Vol. 4, No. 3, September 2002, p. 563 - 568

ELECTRON SPIN RESONANCE OF BAND-EDGE MODULATED AMORPHOUS HYDROGENATED SILICON NITRIDE FILMS

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Band-edge modulated amorphous hydrogenated silicon nitride films are subject to electron spin resonance measurements at room temperature. In these films, the edges of conduction and valence bands are spatially modulated with an almost sinusoidal function along a direction z perpendicular to the deposited layers by varying the nitrogen composition along this direction. The results are discussed in terms of silicon-dangling bonds forming deep centres in the band-gap region.

(Received 20 June 2002; accepted July 22, 2002)

Keywords: Amorphous hydrogened silicon nitride, ESR, Band – edge modulated films

1. Introduction

The band-edge modulated (BM) amorphous hydrogenated silicon nitride (a-$Si_{1-x}N_x$:H) films[1-5] are artificial semiconducting materials in which the edges of conduction and valence bands are spatially modulated with an almost sinusoidal function along a direction z perpendicular to the deposited layer, as shown in Fig. 1. It has been shown that the band-gap energy (optical gap) increases with decreasing the modulation period L from 300 Å to 30 Å, as shown in Fig. 2. This has been concluded to be due to the quantum-size effect in a modulated potential being approximated by a harmonic-oscillator potential [2, 5]

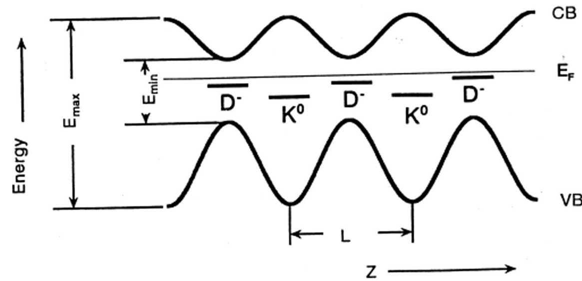

Fig. 1. Schematic diagram of edges of the conduction and valence bands and of the levels of D^- (negatively - charged silicon - dangling bond) and K^0 (neutral silicon – dangling bond in a-Si_3N_4:H) in band-edge modulated a-$Si_{1-x}N_x$:H films. E_F designates the Fermi level.

In this paper, we deal with electron spin resonance (ESR) of deep centres, i.e., silicon-dangling bonds whose energy levels are indicated in the band-gap region in Fig. 1. Silicon-dangling bonds around the region having maximum-band gap as shown in Fig. 1 are neutral ones having either two nitrogen backbond sites (a silicon backbond site) or three nitrogen backbond sites (no silicon backbond sites), while silicon-dangling bonds around the region having minimum-band gap are mostly normal ones having three silicon backbond sites, but most of them are negatively charged because charge transfer occurs from the nitrogen-rich region to the silicon-rich region.

The purpose of this study is to elucidate the nature of silicon-dangling bonds in BM films in comparison with a-$Si_{1-x}N_x$:H alloy films and also in relation to the quantum-size effect observed in the BM films. We present experimental procedures and ESR results in sections 2 and 3, respectively and discuss the results in terms of deep centres, as shown in Fig. 1, in section 4. The conclusions are drawn in section 5.

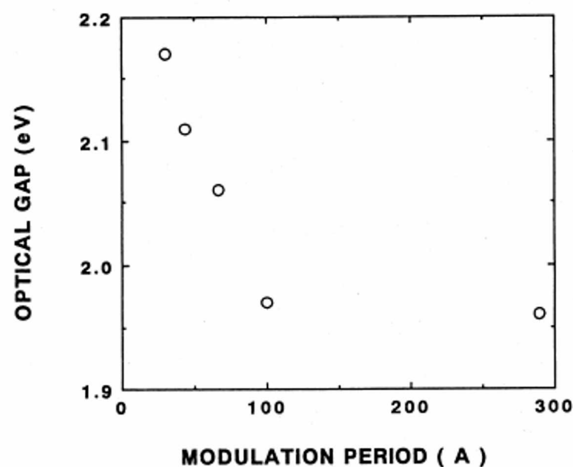

Fig. 2. Optical gap as a function of modulation period in band-edge modulated a-$Si_{1-x}N_x$:H films.

2. Experimental

ESR measurements in BM films and a-$Si_{1-x}N_x$:H alloy films were performed at room temperature, using a conventional ESR spectrometer (JEOL JES-RE1X) operating at 9.4 GHz. The g-value and spin density were estimated by comparison with the ESR signal of TCNQ:Li (g = 2.0026) and by comparison with a standard weak coal sample, respectively.

Samples studied in the present measurements were prepared on fused silica substrates held at 250 ^oC, using a plasma-enhanced chemical vapour deposition technique, in which two types of mixture gas were used, i.e., gas A of a mixture ratio $[SiH_4] : [H_2] = 1 : 9$ and gas B of mixture ratio $[SiH_4] : [H_2] : [NH_3] = 1 : 9 : 10$ [2]. The flow-rate ratio of these gases was controlled by flow controllers with a computer to change sinusoidally, i.e., the ratio of the flow rate F_B of gas B to the sum of $F_A + F_B$ varied sinusoidally in the range between 0.10 and 0.90. $F_A + F_B$ and the pressure inside the reaction chamber were kept at 32 sccm and 0.50 ± 0.02 Torr, respectively. The period T of the flow rate modulation ranged between 35 s and 340 s. The response time of the flow controller and the residence time of gas in the chamber were 1 s and 1.3 s, respectively, so that they were both much shorter than T. The minimum band-gap was 1.91 eV, i.e., the nitrogen composition was not zero, because it was difficult to control the flow rate of gas B exactly to be zero. This band gap corresponds to that of an alloy film No.2513 in Table 1. The maximum band-gap was estimated to be 4.05 eV [2], which is smaller than the optical gap of a-Si_3N_4:H No.2503 (E_g = ~5.0 eV). The modulation period was estimated from period time and deposition rate (For detail, see ref. [2]). The estimated value of the modulation period was consistent with those deduced from X-ray diffraction measurements [6].

The sample characteristics and preparation condition are listed in Table 1, in which the band-gap energy E_g (optical gap) was estimated by using optical transmission and photothermal deflection measurements [2,6]. The optical gap is shown as a function of modulation period in Fig. 2. The result has been accounted for in terms of the quantum-size effect.

Table 1. Characteristics of samples.

Sample No.	Thickness (μm)	Mod.Period (Å)	Period Number	E_g (eV)
6003		30	300	2.17
6004		290	35	1.96
6006		100	100	1.97
6007		44	230	2.11
6008		67	150	2.06
6010		38		
6017		21	600	
2502*	1.16			2.40
2503**	1.38			~5.0
2513	1.06			1.91***

*) a-Si_3N_2:H; Used gas: mixture of SiH_4, N_2 and H_2.

**) a-Si_3N_4:H; Used gas : gas B.

***) photon energy corresponding to $\alpha = 10^3 cm^{-1}$.

3. Results

ESR spectra of BM films and a-$Si_{1-x}N_x$:H alloy films observed at room temperature are shown in Fig. 3. The observed g-value, g, the peak to peak separation, ΔH_{pp}, and spin density, N_S, are given in Table 2 as well as the modulation period. A-$Si_{1-x}N_x$:H alloy films Nos. 2502 and 2503 are a-Si_3N_2:H and a-Si_3N_4:H films, respectively. The observed g-values and spin densities are plotted as a function of modulation period in Figs. 4 and 5, respectively.

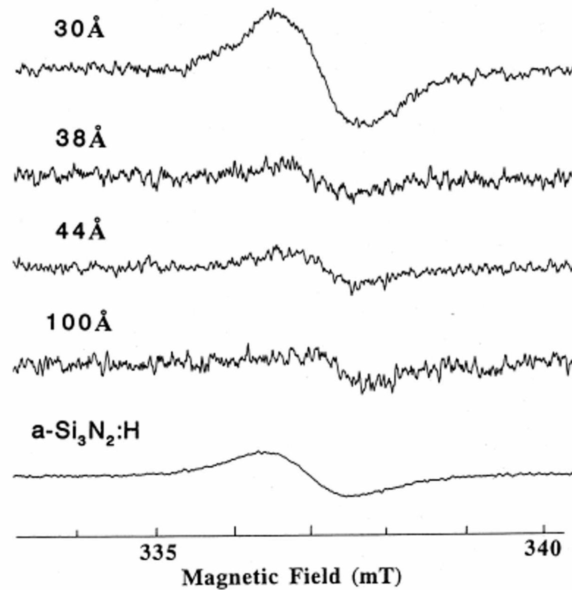

Fig. 3. ESR spectra of band-edge modulated a-$Si_{1-x}N_x$:H films and of a-Si_2N_3:H film. The modulation period is indicated in the figure.

4. Discussion

The magnetic centre responsible for ESR in BM and a-$Si_{1-x}N_x$:H alloy films is assumed to be silicon-dangling bonds. In a-$Si_{1-x}N_x$:H alloy films, the line broadening may be due to hyperfine interaction with nitrogen nuclei at backbond sites [7], in which there are three cases, as shown in Fig. 6(a) – (c): (1) all backbond sites are occupied by nitrogen (Fig. 6(a)), (2) two of backbond sites are occupies by nitrogen (Fig. 6(b)), and (3) one of backbond sites is occupied by nitrogen (Fig. 6(c)). For the case (1), the silicon-dangling bond is called K centre[8]. As shown in Table 2, ΔH_{pp} is 10.3 G for a-Si_3N_2:H alloy film No.2502. ΔH_{pp} is 4.3 G for a-Si_3N_4:H alloy film No.2503. ΔH_{pp} is 8.3 – 9.8 G for BM films. A-Si_3N_4:H has a stoichiometric composition, i.e., it is composed of fourfold-coordinated silicon atoms and threefold-coordinated nitrogen atoms. This indicates that spatial fluctuation of local atomic configuration around a silicon-dangling bond is small compared to other samples, i.e., a-Si_3N_2:H alloy films and BM films, so that g-value fluctuation associated with the above three cases contributes to the line broadening. From the above consideration, the g-value fluctuation also contributes to the line broadening as well as the hyperfine interaction mentioned above.

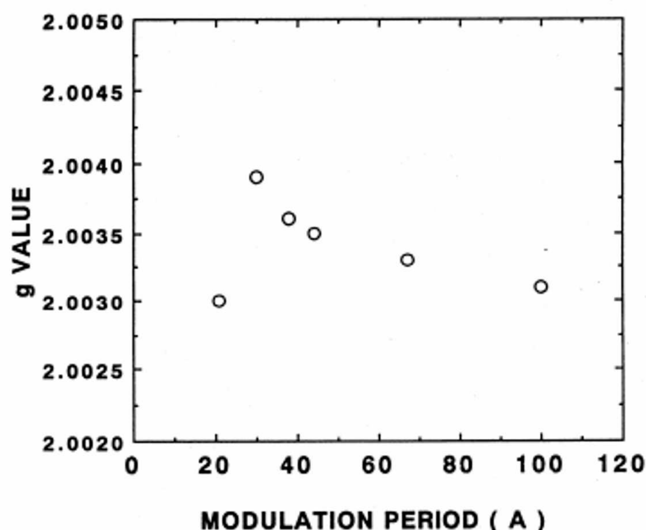

Fig. 4. g-value as a function of modulation period in band-edge modulated a-$Si_{1-x}N_x$:H films.

The observed g-value of BM films ranges between 2.0030 and 2.0039. These values are close to the g-value of K centre in a-Si_3N_4:H (g = 2.0028[8]). This suggests that the backbond sites of the silicon-dangling bond in BM films correspond to the cases (1) and (2) mentioned above. As shown in Fig. 1, most of silicon-dangling bonds seem to be negatively charged around the region corresponding to minimum band-gap (silicon-rich region), because charge transfer occurs from the nitrogen-rich region to the silicon-rich region. On the other hand, neutral silicon-dangling bonds (K^0 centres) exist much in the nitrogen-rich region compared to the silicon-rich region, as shown in Fig. 1. As a result, the g-value of BM films deviates from that of a-Si:H (g = 2.0055) and becomes close to that of a-Si_3N_4:H (K centre, g = 2.0028), as observed in BM films. As seen from Table 2 and Fig. 4, the observed g-value seems not dependent on modulation period within the experimental error of g-values. This indicates that the g-value of BM films is not affected by the quantum-size effect. This is because silicon-dangling bond centres are deep centres, as shown in Fig. 1.

Table 2. The experimental values of ESR parameters.

Sample No.	Modulated period (Å)	g-value	ΔHpp (gauss)	Ns (cm^{-3})
6003	30	2.0039	8.9	7.1×10^{17}
6006	100	2.0031	9.8	3.1×10^{17}
6007	44	2.0035	9.7	4.2×10^{17}
6008	67	2.0033	8.3	1.4×10^{17}
6010	38	2.0036	8.3	1.8×10^{17}
6017	21	2.0030	9.2	3.2×10^{18}
2502		2.0027	10.3	2.4×10^{18}
2503			4.3	

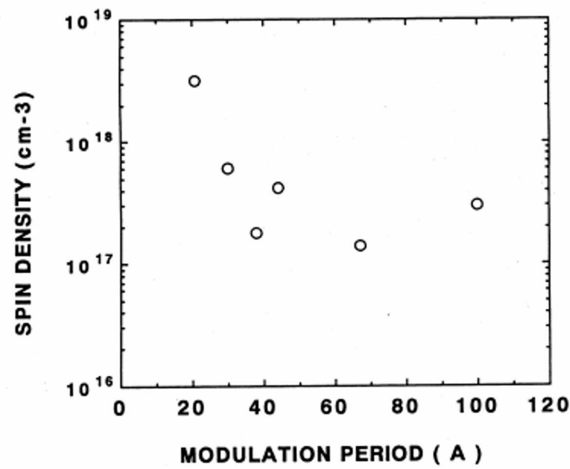

Fig. 5. Spin density as a function of modulation period in band-edge modulated a-$Si_{1-x}N_x$:H films.

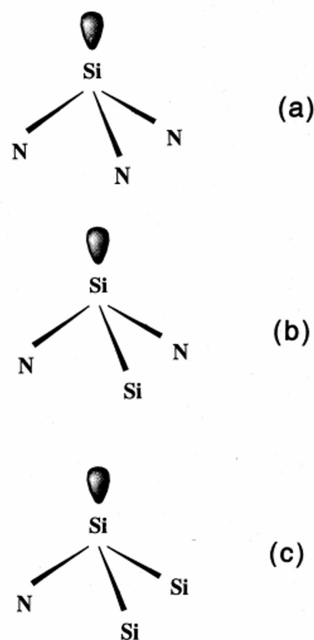

Fig. 6. Atomic configurations of silicon-dangling bonds with (a) three nitrogen backbond sites, (b) two nitrogen backbond sites and (c) one nitrogen backbond site.

This is due to that BM films with short L have rapid variation of nitrogen composition along a direction perpendicular to the deposited plane compared to BM films with long L, so that silicon-dangling bonds may be easily created as a result of wrong bonding-arrangements.

5. Conclusions

We conclude that magnetic centres responsible for an ESR signal observed in BM films are silicon-dangling bonds having either three nitrogen backbond sites or two nitrogen backbond sites.

Most of silicon-dangling bonds around the minimum band-gap region are concluded to be negatively charged as a result of charge transfer from the nitrogen-rich region to the silicon-rich region. The result that the observed g-values in BM films are not dependent on modulation period can be accounted for by considering that silicon-dangling bonds are deep centres. Thus, no quantum-size effect is expected for the g-value in BM films in accordance with the observation.

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