DEFECTS INVESTIGATION IN PHOTO-CVD SILICON NITRIDE FILMS

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ESR and UV/visible spectroscopy were used for defects investigation in silicon nitride thin films prepared by the mercury-sensitized photochemical vapor deposition (photo--CVD) method using SiH_4 and NH_3 gas mixtures. For the films deposited at 250°C ESR signal and optical absorption behavior with varying NH_3/SiH_4 flow rate ratio is shown to be basically similar to that observed in PECVD silicon nitride films.

1. INTRODUCTION

Recently, the mercury-sensitized photochemical vapor deposition (photo-CVD) of silicon nitride has been reported to yield thin films with good properties for various applications in the microelectronics industry /1-4/. The potential advantages of this method are low deposition temperature, no irradiation damage of deposited film and/or underlying substrate, and good step coverage. However, photo-CVD silicon nitride films have not been studied so exstensivelly as the films prepared by PECVD (plasma-enhanced chemical vapor deposition) process.

In this paper the results of defects investigation by electron spin resonance (ESR) and UV/visible spectroscopy are presented for silicon nitride films prepared by mercury-sensitized photo-CVD method using SiH_4 and NH_3 gas mixtures.

2. EXPERIMENTAL

The design of photo-CVD reactor used in this study is basically the same as for photo-CVD reactors described elsewhere /2,4/. Fused quartz substrates were used to deposit samples for both ESR and UV/visible measurements. An X-band Varian E 109 system was used for ESR measurements at room temperature. Preparation conditions for samples studied are given in Table 1.

Table 1. Preparation conditions.

Sample number	Flow rate (sccm)			NH_3/SiH_4 ratio(R)	T_s (^oC)	Growth rate (nm/min)
	SiH_4	NH_3	Total			
38	3	12	15	4.00	250	1.33
39	3	22	25	7.33	250	2.00
40	3	37	40	12.33	250	2.66

3. RESULTS AND DISCUSSION

The results of ESR measurements are presented in Figure 1. As can be seen, spin density (Ns) and g-value decrease while linewidth (ΔHpp) increases with increasing NH_3/SiH_4 flow rate ratio (R). Under reasonable assumption that by increasing R the nitrogen content of deposited films is also increased it can be stated that photo-CVD films behave much the same way the PECVD silicon nitride films do, as far as g-value and linewidth are concerned /5-8/. The explanation of such behavior could be that linewidth increases with increasing nitrogen content because of the hyperfine structure caused by the ^{14}N nuclear spin, and the g-value decreases because of the interaction of silicon dangling bonds with surrounding nitrogen atoms /9/. However, regarding

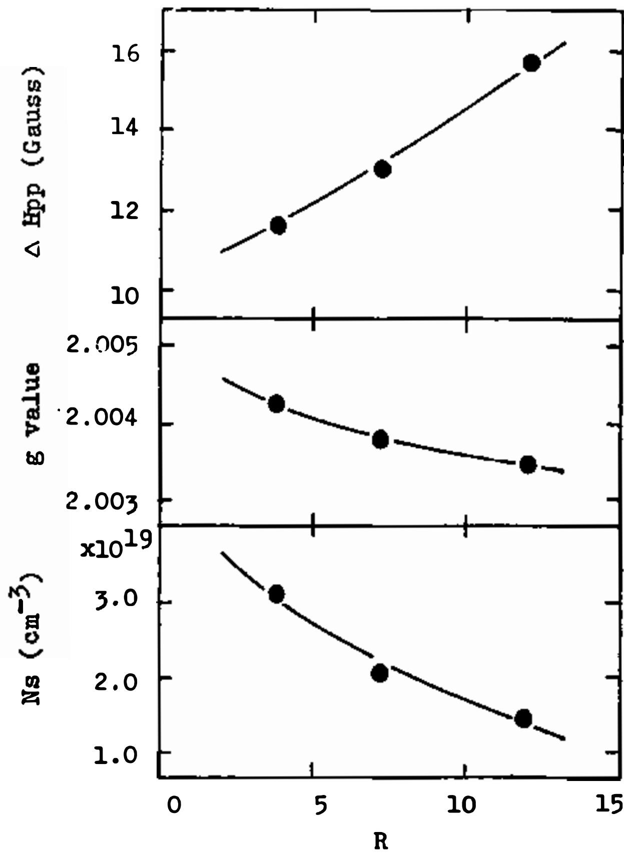

Fig. 1. The results of ESR measurements.

the spin density photo-CVD films are clearly inferior in comparison with PECVD silicon nitride /6-8/. The reason for that might be the very nature of photo-CVD process because during the deposition growing film is permanently exposed to strong UV illumination which is known to largely increase the spin density of silicon nitride films /9/.

By measuring the optical absorption of photo-CVD films it was possible to obtain values for optical band gap (E_g) of these samples using the well-known expression:

$$\alpha h\nu = B(h\nu - E_g)^2, \qquad (1)$$

where α is the absorption coefficient and $h\nu$ the photon energy.

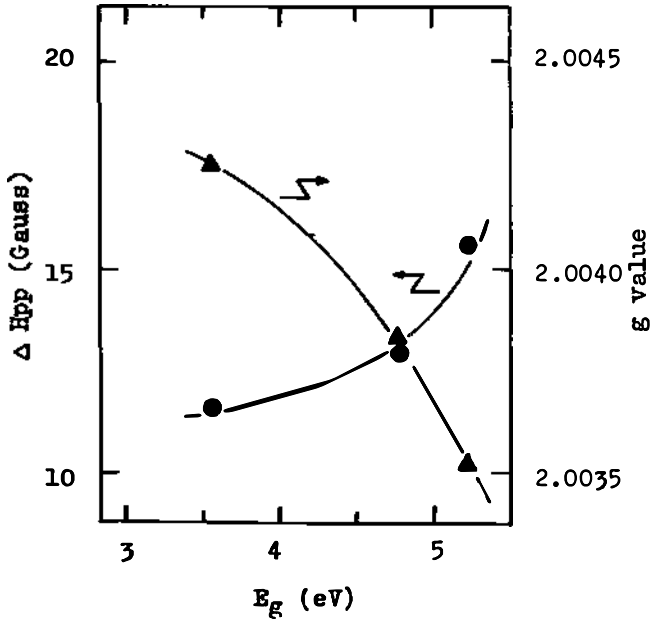

Fig. 2. ESR linewidth and g-value as a function of the optical band gap.

As in the case of PECVD silicon nitride films /5-7/ the value of optical band gap increases with increasing R. Figure 2. shows ESR linewidth and g-value as a function of optical band gap for photo-CVD samples but similar results have already been published for PECVD silicon nitride /7/.

ACKNOWLEDGEMENTS The author is indebted to Prof. Tatsuo Shimizu and the staff of his laboratory at Kanazawa University (Japan) where the main part of this work has been done for continuous encouragement and support.

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