

Invited

Defects in Amorphous Silicon-Nitrogen Alloy Films

Tatsuo SHIMIZU

Department of Electrical and Computer Engineering, Faculty of Engineering,
Kanazawa University, Kanazawa 920, Japan

Various kinds of defects in amorphous silicon-nitrogen alloy films investigated by electron-spin-resonance (ESR) and light-induced changes in ESR are reviewed. Furthermore microscopic models for various ESR centers are identified by a comparison with the results of a computer calculation.

1. INTRODUCTION

Nature of defects in hydrogenated amorphous silicon-nitrogen alloy ($a\text{-Si}_{1-x}\text{N}_x\text{H}$) films has been studied by many authors since Yokoyama *et al.* reported the results of ESR measurements for the first time in 1981.¹⁾ Soon after that, systematic ESR studies for these films with various nitrogen contents x and theoretical interpretations were carried out by the present author in 1982.^{2, 3)} In this talk, I will make an overview of the present understanding of defects in $a\text{-Si}_{1-x}\text{N}_x\text{H}$ with various values of x .

2. SI DANGLING BONDS

The peak-to-peak linewidth ΔH_{pp} and the g -value of the ESR signal are shown in Fig. 1 against the N content for $a\text{-Si}_{1-x}\text{N}_x$ and $a\text{-Si}_{1-x}\text{N}_x\text{H}$ prepared by magnetron sputtering²⁾ and glow discharge deposition.⁴⁾ Dashed curves shown in this figure are the calculated ΔH_{pp} and g . The calculations were carried out by using the extended Hückel theory (EHT) for small clusters with varying compositions by assuming that the ESR signal arises from Si dangling bonds.³⁾ The fact that the calculated ones agree fairly well with the observed ones suggests that the ESR signal arises from Si dangling bonds. ΔH_{pp} increases with an increase in x because of the appearance of unresolved hyperfine splitting due to ^{14}N nuclei located neighboring to the Si atom with the dangling bond. The g -value decreases with x mainly because the energy separation between a bonding level and an antibonding level for the Si-N bond is larger than that for the Si-Si bond. Later Lenahan *et al.* observed ^{14}N nearest neighbor hyperfine interactions and ^{29}Si hyperfine interactions with an unpaired electron on Si dangling bond centers using both electron-nuclear-double-resonance (ENDOR) and weak satellite lines in ESR spectra.^{5, 6)} Ishii and myself made *ab initio* calculations for these hyperfine interaction parameters using the density functional theory and the fairly good agreement between the observed values and the calculated values were obtained.⁷⁾ The fact further verifies the above mentioned assignment.

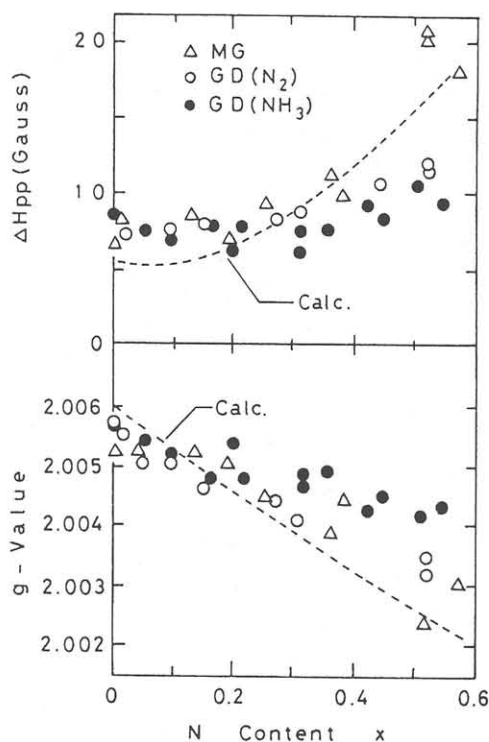


Fig. 1. Peak-to-peak linewidth ΔH_{pp} and g -value for $a\text{-Si}_{1-x}\text{N}_x$ and $a\text{-Si}_{1-x}\text{N}_x\text{H}$ prepared by magnetron sputtering (MG), glow discharge deposition of SiH_4 and N_2 (GD(N_2)) and of SiH_4 and NH_3 (GD(NH_3)).⁴⁾ Dashed curves show corresponding calculated ones.

3. NITROGEN DANGLING BONDS

Until Warren *et al.* observed the ESR signal from nitrogen dangling bonds, no nitrogen-related defects had been observed.⁸⁾ Since nitrogen has a nucleus spin, the ESR signal originating from nitrogen-related defects should exhibit a hyperfine structure. The ESR signal with a hyperfine structure was observed by Warren *et al.* in the N-rich $a\text{-Si}_{1-x}\text{N}_x\text{H}$ films after a high temperature ($> 500^\circ\text{C}$) anneal followed by UV irradiation. The ESR signal was fitted by a computer analysis using $g_{\parallel} = 2.003$, $g_{\perp} = 2.0053$ and $A_{\parallel} = 30.5\text{ G}$, $A_{\perp} = -4.75\text{ G}$.⁹⁾ Here g_{\parallel} and g_{\perp} are the components of the g -tensor and A_{\parallel} and A_{\perp} are the components of the hyperfine tensor. Ishii and myself calculated the corresponding hyperfine

constants for the nitrogen dangling bond in a Si-N cluster using the density functional theory with a local-spin-density approximation.^{7, 10)} The calculated ¹⁴N hyperfine parameters agree fairly well with those observed by Warren *et al.*, confirming the ESR center to be a twofold coordinated N atom.

4. N-PAIR DEFECTS

ESR spectra in N-rich a-Si_{1-x}N_xH sometimes exhibit some structures. However the origin of the structure had been not clear until the detailed experimental^{11, 12)} and theoretical¹³⁾ investigations were carried out in our group. Figure 2 shows an example of such a spectrum. It was found that a complicated ESR spectrum such as shown in Fig. 2 appears when N-rich a-Si_{1-x}N_xH films are prepared at a high deposition rate. Furthermore it was found that these films with the complicated ESR spectrum have a smaller *B* value in the Tauc plot of the optical absorption. A smaller *B* value is known to show a larger randomness in the network structure. We also analysed the ESR spectra using the isotope ¹⁵N. As a result, it was verified that the complicated structure in the ESR spectrum originates from the hyperfine interaction with N nuclei. However the spectrum is different from that of N dangling bonds described in section 3. With comparison of the observed ESR spectrum with the results of a computer simulation and an *ab initio* calculation using the density functional theory, the spectrum was confirmed to originate from N-pair defects. Such an N-pair defect has a close

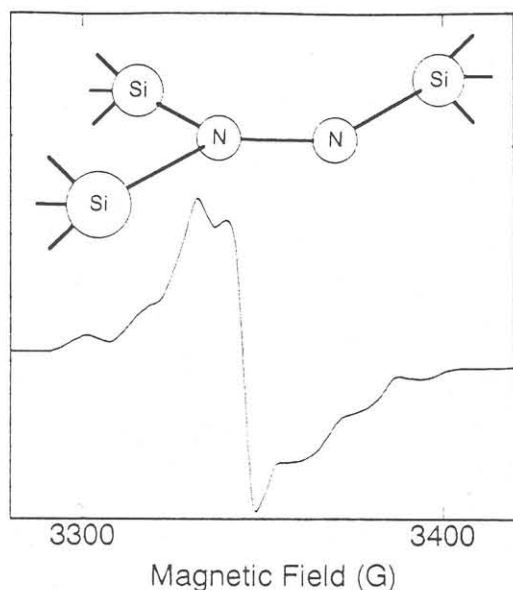


Fig. 2. ESR spectrum for N-pair defect in N-rich a-Si_{1-x}N_xH. N-pair defect model is also shown in the figure.¹²⁾

resemblance with peroxy radical in SiO₂ glass (Si-O-O•)¹⁴⁾ and one kind of S dangling bonds in S-rich amorphous Ge-S (Ge-S-S•)¹⁵⁾ both observed by ESR.

5. LIGHT-INDUCED ESR

Light-induced ESR (LESr) in a-Si_{1-x}N_xH was observed for the first time in our group in 1984.¹⁶⁾ Thereafter a lot of investigations on LESr in a-Si_{1-x}N_xH have been carried out by Kanicki *et al.*¹⁷⁾ However the origin of the LESr has been still controversial. We suggested that the LESr arises from the photoexcited-carrier capture at charged defects N₄⁺ and Si₃⁻.¹⁸⁾ It was assumed that the N₄⁺ changes into N₃⁰ and the neighboring Si₄⁰ changes into Si₃⁰ after capturing the electron at the N₄⁺. A small fraction of N atoms were assumed to have a fourfold coordination with a positive charge, that is, N₄⁺. On the other hand, Kanicki *et al.* proposed that defects in a-Si_{1-x}N_xH have a negative effective electron correlation energy, producing Si₃⁺ and Si₃⁻ in thermal equilibrium.¹⁷⁾ For N-rich a-Si_{1-x}N_xH, the LESr was found to originate from the carrier capture at charged defects by judging from the combination of LESr and capacitance-voltage (*C-V*) measurements.¹⁹⁾ The LESr signal in these N-rich a-Si_{1-x}N_xH films was found to be photobleached by subgap illumination,²⁰⁾ which also supports the carrier-capture model for the LESr.

Rather recently, Fritzsche and Nakayama proposed an alternative explanation for the stabilization of charged defects.^{21, 22)} Large potential fluctuations caused by the incorporation of N atoms into a-Si:H causes some of the defects to be charged. Our recent results of the relationship between electrical conductivity and charged-dangling-bond density in N- and P-doped a-Si:H suggest that our previous N₄⁺ model for the origin of the LESr in a-Si_{1-x}N_xH appears to be invalid and that the potential-fluctuation model proposed by Fritzsche *et al.* appears to be more preferable.²³⁾

In a-Si_{1-x}N_xH with *x* of 0.3 ~ 0.5, we found the presence of two kinds of LESr signals both at room temperature and 77 K.²⁴⁻²⁶⁾ Both kinds of the LESr signal have the same signal as the dark ESR signal. One kind of the signal grows very rapidly with illumination while the other grows very slowly. We will call them the fast-process dangling-bond (FPDB) and the slow-process dangling-bond (SPDB), respectively. Figure 3 shows examples of the spin density increment ΔN_s under illumination against illumination time. The FPDB is thought to be produced by the carrier capture at the charged dangling bond, while the SPDB is thought to be produced by the bond breaking. It is found that the FPDB can be photobleached by subgap illumination while the SPDB can not be photobleached.²⁶⁾ It is also found that the FPDB is thermally-annealed with a smaller annealing-activation-energy around 0.43 eV while the

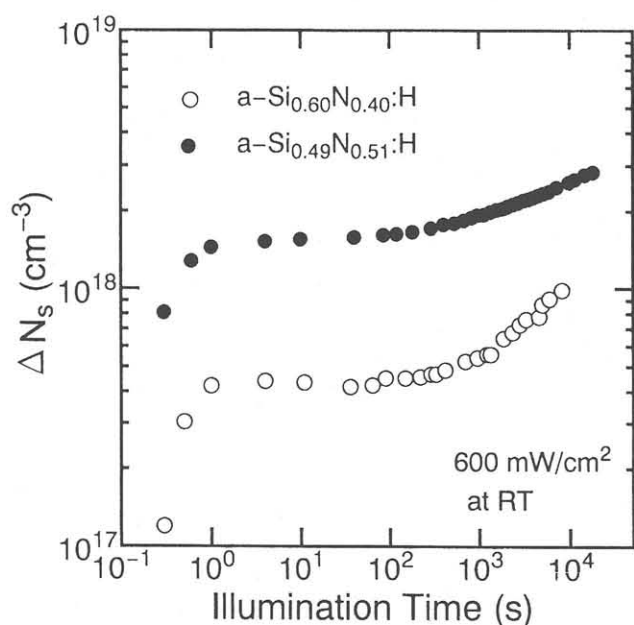


Fig. 3. Examples of the spin density increment ΔN_s under illumination against illumination time for $a\text{-Si}_{1-x}\text{N}_x\text{H}$.

SPDB is thermally-annealed with a larger annealing-activation-energy around 1.1 eV.²⁷⁾ These results support the idea that the FPDB is produced by the carrier capture while the SPDB is produced by the bond breaking.

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References

- 1) S. Yokoyama, M. Hirose and Y. Osaka: Jpn. J. Appl. Phys. **20** (1981) L35.
- 2) T. Shimizu, S. Oozora, A. Morimoto, M. Kumeda and N. Ishii: Solar Energy Mater. **8** (1982) 311.
- 3) N. Ishii, S. Oozora, M. Kumeda and T. Shimizu: Phys. Status Solidi **b114** (1982) K111; Erratum *ibid* **135** (1986) K169.

- 4) A. Morimoto, Y. Tsujimura, M. Kumeda and T. Shimizu: Jpn. J. Appl. Phys. **24** (1985) 1394.
- 5) P. M. Lenahan and S. E. Curry: Appl. Phys. Lett. **56** (1990) 157.
- 6) W. L. Warren and P. M. Lenahan: Phys. Rev. **B42** (1990) 1773.
- 7) N. Ishii and T. Shimizu: Mater. Res. Soc. Symp. Proc. **258** (1992) 305.
- 8) W. L. Warren, P. M. Lenahan and S. E. Curry: Phys. Rev. Lett. **65** (1990) 207.
- 9) W. L. Warren, F. C. Rong, E. H. Poindexter, G. J. Gerardi and J. Kanicki: J. Appl. Phys. **70** (1991) 346.
- 10) N. Ishii and T. Shimizu: Phys. Rev. **B44** (1991) 12776.
- 11) M. Kumeda, N. Awaki, H. Yan, A. Morimoto and T. Shimizu: J. Non-Cryst. Solids **137/138** (1991) 887.
- 12) H. Yan, M. Kumeda, N. Ishii and T. Shimizu: Jpn. J. Appl. Phys. **32** (1993) 876.
- 13) N. Ishii and T. Shimizu: Phys. Rev. **B48** (1993) 14653.
- 14) D. L. Griscom: J. Ceram. Soc. Jpn. **99** (1991) 923.
- 15) I. Watanabe, M. Ishikawa and T. Shimizu: J. Phys. Soc. Jpn. **45** (1978) 1603.
- 16) M. Kumeda, H. Yokomichi and T. Shimizu: Jpn. J. Appl. Phys. **23** (1984) L502.
- 17) J. Kanicki, W. L. Warren, C. H. Seager, M. S. Crowder and P. M. Lenahan: J. Non-Cryst. Solids **137/138** (1991) 291.
- 18) T. Shimizu, H. Kidoh, A. Morimoto and M. Kumeda: Jpn. J. Appl. Phys. **28** (1989) 586.
- 19) J. Kanicki, M. Sankaran, A. Gelatos, M. S. Crowder and E. D. Tober: Appl. Phys. Lett. **57** (1990) 698.
- 20) E. D. Tober, M. S. Crowder and J. Kanicki: Mater. Res. Soc. Symp. Proc. **192** (1990) 725.
- 21) H. Fritzsche and Y. Nakayama: Philos. Mag. **B69** (1994) 359.
- 22) H. Fritzsche: Appl. Phys. Lett. **65** (1994) 2824.
- 23) A. Masuda, K. Itoh, J. -H. Zhou, M. Kumeda and T. Shimizu: Jpn. J. Appl. Phys. **33** (1994) L1295.
- 24) M. Kumeda, A. Sugimoto, J. Zhang, Y. Ozawa and T. Shimizu: Jpn. J. Appl. Phys. **32** (1993) L1046.
- 25) M. Kumeda, A. Sugimoto, J. Zhang, Y. Ozawa and T. Shimizu: J. Non-Cryst. Solids **164-166** (1993) 1065.
- 26) J. Zhang, Q. Zhang, M. Kumeda and T. Shimizu: Phys. Rev. **B51** (1995) 2137.
- 27) J. Zhang, Q. Zhang, M. Kumeda and T. Shimizu: Mater. Res. Soc. Symp. Proc. **377** (1995) in press.

