Mechanisms of intrinsic stresses generation in sputtered amorphous Si : H films

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(Received 14 November 1994; accepted 29 June 1995)

The relation between stresses of sputtered *a*-Si : H films and the film deposition conditions are investigated. The film stresses change from a large compressive stress of 1000 MPa to an almost stress-free one. They arise from distortions of the Si network via the following two mechanisms. The first results from the inclusion of the Ar-sputtering gas into the films, which provides volume expansion of the film network. The other is due to structural disorders, such as a deviation of the Si bond angle which is generated during the deposition processes. Moreover, it is found that Si–H terminations in the films contribute to reducing the film stresses because the Si–H termination breaks and relaxes the Si network. These effects can be realized as long as the Si–H terminations are homogeneously distributed in the films.

I. INTRODUCTION

In the integration of various optical components, a technique of direct insertion of optical devices into optical fibers has attracted attention.[1, 2] In such cases, these devices must be small in size. A miniaturized optical isolator, including multilayered polarizers, is proposed by Siraishi and Kawakami to fabricate laser modules.[3] They also reported that multilayers composed of *a*-Si : H and SiO_2 films prepared by a sputtering method, which are named "Laminated Polarization Splitters (LPS)", can be applicable to such polarizers.[3] In the fabrication of LPS, to ensure ease of adjustment of its position, it is desirable to increase the total thicknesses of the LPS-multilayers. However, thick multilayers are mechanically weak and fracture easily due to their large film stresses. Therefore, in the fabrication of multilayers, a reduction of film stresses is the key technique in the achievement of mechanically strengthened structures.

In the present study, the relation between stresses of sputtered Si : H films and their deposition conditions was investigated in order to obtain thick LPS multilayers. As a result, the conditions resulting in fabrication of stress-free films were determined. Further, origins of the sputtered Si : H film stresses are discussed in terms of the film composition and structure.

II. EXPERIMENTAL

The Si : H films were prepared in a magnetron rf-sputtering chamber. A nondoped crystalline Si was used as a sputtering target with a distance to the substrate of 120 mm. An Ar/H_2 mixture at the flow rate of 120 sccm was used as the sputtering gas. The sputtering conditions (sputtering pressure, rf-power and substrate temperature) are listed in Table I. Internal stresses of the Si : H films were measured for 1-μm-thick samples deposited on 3 inch Si(100) wafers, according to the method reported by Mack and Reisman.[4] Ar contents and Si densities in the films were determined by a Rutherford back scattering spectroscopy (RBS). Bonded H contents in the films were estimated by an elastic recoil detection (ERD) method using incident He^{++}. In the present study, the amounts of H determined by the ERD method were taken to be the concentration of bonded H, because the amounts of H forming into H_2 molecules in Si : H films are less than 1 at. %.[5] Carbon plates were used as substrates in both RBS and ERD measurements. Densities of dangling bonds (*Nd*) in the films, with coplanar aluminum electrodes on the top surface, were measured using a constant photocurrent method (CPM). The value of the calibration constant of CPM was taken to be 1×10^{16} cm^{-2}.[6] Si network structures of these films were investigated by both Raman and Fouriertransform infrared transmission (FTIR) spectroscopies.

TABLE I. Sputtering conditions of the Si : H films.

Sputtering pressure	(P_T)	0.20 – 0.67 (Pa)
RF power	(P_W)	375 – 750 (W)
Sputtering gas		Ar/H_2 120 sccm
H_2 gas flow ratios	(F_H)	5 – 15 (%)
Substrate temperature	(T_S)	RT – 200 (°C)

III. RESULTS

The internal stresses, Ar and bonded H contents, densities of Si atoms, and *Nd* values of the samples prepared under various deposition conditions (only the sputtering pressure was kept at 0.67 Pa) are shown in Fig. 1. No Si–OH bonds around 3650 cm^{-1} were detected by the FTIR measurements in any of the samples. The internal stresses of the films deposited at 200℃ were smaller than those of the films deposited at ambient temperature and were changed from compressive to tensile at an H_2 flow ratio of 15% [Fig. 1(a)]. Further, we found the film deposited at lower pressure, 0.2 Pa, exhibited a large compressive stress of 1000 MPa (Table II). The amounts of Ar in the films were not influenced by changing the substrate temperature from ambient temperature to 200℃, when other deposition conditions were kept unchanged [Fig. l(b)]. Films included large amounts of bonded H, resulting from the conditions under lower substrate temperatures and rf powers, as observed at an H_2 gas flow ratio of 5% [Fig. l(c)]. However, *Nd* values in the films deposited at *Ts* = 200℃ were small compared to those deposited at ambient temperatures. Unfortunately, the *Nd* values of the films prepared at ambient temperature were not measured, because of large amounts of *Nd* in the films which made it impossible to be determined by CPM. The densities of Si atoms in the films increased with both the increasing substrate temperature and the rf power, and decreased with the increasing H_2 gas flow ratios [Fig. l(d)].

The Raman spectra of the samples are shown in Fig. 2. A Raman spectrum for Si consists of four bands, TA, LA, LO, and TO.[7] It is well known that a TO band (main peak) is about 520 cm^{-1} for crystalline Si (*c*-Si), while it shifts to about 480 cm^{-1} for amorphous silicon (*a*-Si).[8] In addition, a FWHM of the TO band (ΔTO) is varied by changing the distribution of the Si–Si bond angle, and it increases with an increase in the deviation of the bond angle distribution ($\Delta\theta$).[9, 10] In our samples, the TO band was about 480 cm^{-1} for all films, indicating that the structures of the samples were amorphous. ΔTO values of these films, however, were varied so that the samples had different degrees of structural disorders (Table II).

IV. DISCUSSION

In the present study, we found that the internal stresses of sputtered *a*-Si : H films depend heavily on the deposition conditions. The film stresses were changed from a large compressive stress of 1000 MPa to an almost stress-free (slightly tensile) one. We fabricated a 350-μm-thick multilayer with a film-thickness period of 70 nm with no fractures.[11] This multilayer was composed of the stress-free Si–H film obtained in the present study and hydro-

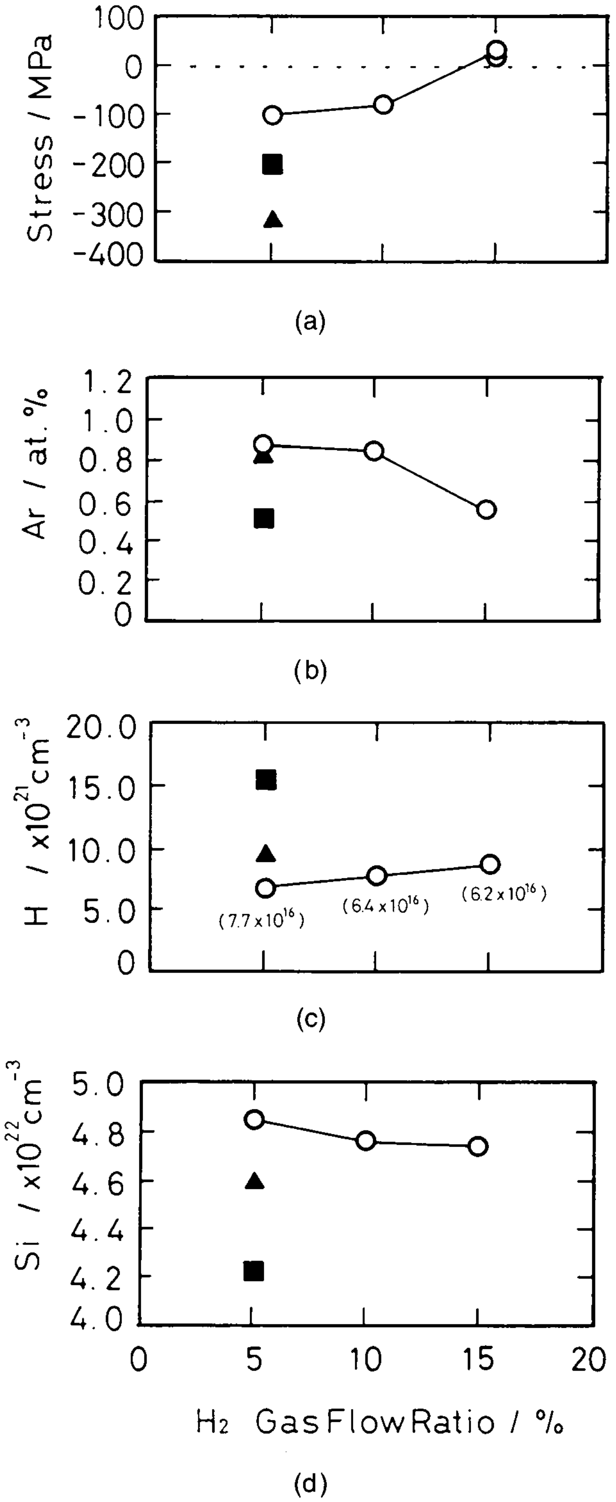

FIG. 1. (a) Relation between the stresses of the Si : H films sputtered at various deposition conditions (only sputtering pressure was fixed at 0.67 Pa) and the H_2 gas flow ratios in Ar/H_2 mixture (120 sccm) : (○) *Ts* = 200℃ and rf 750 W, (▲) *Ts* = ambient temperature and rf 750 W, and (■) *Ts* = ambient temperature and rf 375 W. Relation between the film composition (b) Ar, (c) bonded H, and (d) Si concentration in the films and H_2 gas flow ratios. Values inside parentheses in (c) indicate the densities of dangling bonds (*Nd*) in the films.

TABLE II. Internal stresses and characteristics of Raman-TO peak of the Si : H films. The negative sign of the stress values means that measured internal stress is compressive.

	Deposition parameters					Raman measurements		
No.	P_W (W)	P_T (Pa)	H_2 gas (%)	*Ts* (°C)	Internal stress (MPa)	TO frequency (cm^{-1})	TO FWHM (cm^{-1})	$\Delta\theta$ (deg)
1	750	0.20	5	RT	−1050	478.7	75.0	10.0
2	750	0.67	5	200	−100	478.0	71.3	9.4
3	750	0.67	15	200	17/33	479.7	68.2	8.9

genated silicon oxide film with a compressive stress of 100 MPa. It is also confirmed that such a 200-μm-thick multilayer could not be achieved using an *a*-Si : H film with a compressive stress of 160 MPa.

We discuss origins of film stresses of the sputtered *a*-Si : H film, in conjunction with other previously reported results. First, the intrinsic stress of *a*-Si : H film deposited at 200℃ on an Si wafer is estimated. Next, factors that influence the film stresses are described.

A. The intrinsic stress of *a*-Si : H film

It is necessary to know the intrinsic film stresses in order to determine the mechanisms of film stress induction. The internal stress (σ_t) of a film is the sum of the intrinsic stress (σ_i) and the thermal stress (σ_{th}): thermal stress originates from the differential thermal expansion between the film and the substrate,

$$\begin{aligned}\sigma_t &= \sigma_i + \sigma_{th}\\ &= \sigma_i + (\alpha_s - \alpha_f)\,[E_f/(1 - v_f)]\,(T_s - T_m),\end{aligned}$$

where α_s and α_f are thermal expansion coefficients of the substrate and the Si : H film, respectively. E_f is Young's modulus of Si : H, v_s is Poisson's ratio of Si : H, and T_s and T_m are deposition and measurement temperatures.[12] In the estimation of thermal stress of the Si : H film deposited at 200℃, the values used in calculations were $v_f = 0.28$, $E_f = 4.4 \times 10^4$ MPa, $a_s = 4.6 \times 10^{-6}$ ℃$^{-1}$, $a_f = 4 \times 10^{-6}$ ℃$^{-1}$, $T_s = 200$℃, and $T_m = 25$℃.[13] From these calculations, the thermal stress of the films was estimated to be 6 MPa (tensile). Therefore, the intrinsic stresses of the films deposited at 200℃ were smaller than those of the films deposited at the ambient temperature.

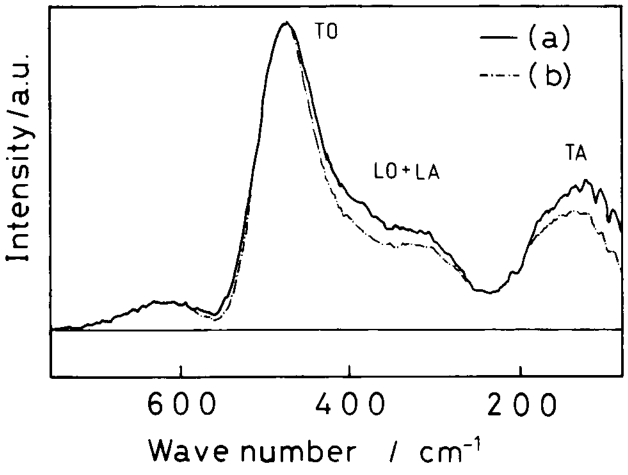

FIG. 2. Raman spectra of the Si : H films deposited at (a) rf 750 W, 0.20 Pa, *Ts* = ambient temperature, and H_2 = 5%, and at rf 750 W, 0.67 Pa, *Ts* = 200℃, and H_2 = 15%. The spectra were all normalized by the TO peak.

B. Influence of Ar contents in films on sputtered film stresses

Many investigators have reported that internal stresses of sputtered films depend on the Ar content in films which is included during the deposition processes.[14, 15] This is known as the peening effect; the inclusion of Ar in the film results in the occurrence of structural distortion. Such distortion induces the internal stress of thin films. Amounts of Ar included in sputtered films tend to increase with deposition at lower pressures.[16, 17] We confirmed the large 1000 MPa of the internal stress of the Si : H film deposited at 0.20 Pa; this condition allows the inclusion of an about 10 times larger Ar amount into the film compared to those deposited at 0.67 Pa. On the other hand, lowerdensity films are generally known to exhibit small stresses.[18, 19] Internal stresses of sputtered Si : H films are, therefore, decreased with decreasing Ar and Si densities of films. Concerning the films deposited at 200℃, in the present study, the relations between stresses and Ar concentration and, similarly, between stresses and Si densities of the films, are in good agreement with the earlier reports.[14, 15]

In order to verify that film stresses arise from the above expected distortion of the structural network, the relation between the stresses and structural disorder of the Si : H films was investigated. Using the ΔTO values obtained from the results of the Raman spectroscopy measurements, the $\Delta\theta$ of the Si–Si bond angles were estimated according to the method reported by Beeman *et al.*[20] (Table II). In Table II, the $\Delta\theta$ values increased with the increase in both film stresses and Ar contents in the films. These results experimentally demonstrated that variations of the $\Delta\theta$ were related to the degree of the distortions in the Si network and support the mechanism of the film stress induction suggested in earlier reports.[14, 15] However, it is noted that the stresses of the films deposited at 200℃ were small compared with those of the films deposited at ambient temperature, although the film deposited at 200℃ was denser and indicated almost the same amount of Ar as the films deposited at ambient temperature (see Fig. 1). Hence, only Ar included in the films did not lead to distortion of the Si network, as discussed later.

C. The role of bonded H for reduction of Si : H film stresses

Bonded H in Si : H films probably breaks and relaxes the Si network. Therefore, a reduction of film stress is expected by the formation of Si–H bonds, although incorporated Ar in the films applied excessive distortions (stresses) to the films. In our previous study, stress-reduced hydrogenated silicon oxide films prepared by an Ar/H_2 sputtering method were achieved by taking the above consideration into account.[21] In the present study, however, although the films deposited at ambient temperature included large amounts of H compared to those of the films deposited at 200℃, the stresses of the films deposited at ambient temperature were larger than those of the films deposited at 200℃. These results indicated that the increase in the amount of bonded H simply led to the reduction of the Si : H film stresses. This inconsistency, with the case of the stresses of the hydrogenated silicon oxide films mentioned above, can be explained in terms of distribution of Si–H bonds in the films.

Table III shows the $(SiH_2)n$ amounts. These structures are formed due to crowd distributions of bonded H in films.[22] The $(SiH_2)n$ amounts are presented as the peak area ratios of the IR spectra at 845 cm^{-1} for $(SiH_2)n$ to the one at 890 cm^{-1} for $SiH_2 + (SiH_2)n$. The film deposited at rf 375 W, ambient temperature, and $H_2 = 5\%$ (film A) included almost the same amount of bonded H as the one deposited at rf 750 W, 200℃, and $H_2 = 15\%$ (film B). However, film A included larger amounts of $(SiH_2)n$ compared with those in film B. Considering that film A exhibited large stress compared to that of film B (which exhibited the smallest film stress), the bonded H forming $(SiH_2)n$ structures did not contribute to a relaxation in the distortion of the Si network. It is also noted that the IR peak assigned to Si–H_3 stretching mode appeared at 2140 cm^{-1} in film B (Fig. 3). Such a peak was not found in other films. The Si–H_3 bond of film B was probably due to the formation of a homogeneous distribution of bonded H in the Si network, because film B included smaller amounts of $(SiH_2)n$ structures, suggesting that the degree of distribution of the Si–H bonds in the film is one of the important factors affecting a reduction of the film stress; homogenous Si–H bond distributions are desirable to achieve less stress in films. Such differences of the distribution of Si–H bonds are caused mainly by changing the substrate temperatures. The distribution of Si–H bonds in the films deposited at low temperatures tends to be inhomogeneous. This is accepted by many investigators.[22, 23]

TABLE III. Amounts of (Si : H_2)nn chain in the Si : H films. The (Si : H_2)n amounts are presented as the ratios of IR peak area at 845 cm^{-1} for (Si : H_2)n to that of 890 cm^{-1} for $SiH_2 + (SiH_2)n$. F_H means a flow ratio of H_2 gas in sputtering gas.

	F_H (%)		
Ts (°C)	5	10	15
RT	0.70	0.66	0.62
200	0.50	0.39	0.29

D. The effect of film-growth processes on film stresses

The substrate temperature also affects the degrees of distortions in the film network structures; such distortions are induced during film-growth processes. Reactive sputtering processes by an Ar/H_2 mixture for preparation of Si : H films produce hydride species, SiH_x, in plasma.[24] The SiH_x species absorbed on a grown film surface diffuse and settle down to the sites that are stabilized from an energy point of view. Consequently, the films are grown, keeping the same Si bond distance and angle as *c*-Si. Actually, the microcrystalline Si : H films prepared by a reactive sputtering method using an Ar/H_2 mixture were reported in Ref. 25. On the other hand, where the species were insufficiently diffused on the film surface, the grown films became amorphous. The previous structural studies of *a*-Si and *a*-Si : H films pointed out that the nearest-neighbor bond distance r_1 of amorphous silicon is not changed compared to that of *c*-Si, and the difference between *c*-Si : H (*c*-Si) and *a*-S : H (*a*-Si) is found in the second neighbor bond distance r_2.[26–28] This difference is due to a deviation of the Si bond angle. The distortions are easily accumulated in the amorphous network, because freedom of a tetrahedral-structure with a deviation of bond angle is subject to a large restriction.[29, 30] One of the reasons for the origins of dangling bonds (Nd) is because of the structural relaxation of the films, as pointed out by Shimizu.[31] He reported that widths of Raman-TO bands of $Si_{1-x}M_x$: H (M = N and C) films, prepared by both reactive sputtering and glow discharge decomposition methods, increase with the increasing Nd values of these films. He concluded that the dangling bonds of the films are produced by a relaxation of the local strains caused by differences of both Si–Si and Si–M bond distances. Crystalline Si : H films should exhibit small stresses because they include less distortions in the film network. Therefore, in order to achieve

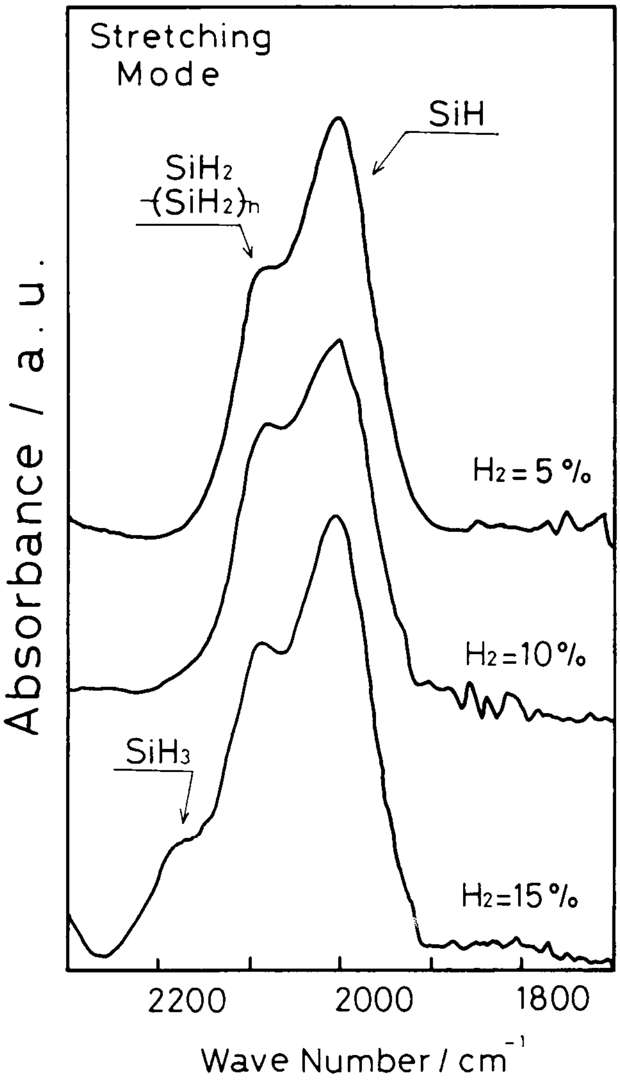

FIG. 3. IR absorption spectra of the Si : H films. All samples were deposited at rf 750 W, 0.67 Pa, and Ts = 200℃. H_2 gas flow ratios were changed from 5 to 15%.

films with less distortion, it is desirable that the substrate temperatures be high, because the surface mobility of the Si : H_x species are proportional to exp $(-E/kT)$, where E is the activation energy of the species for the diffusion, k is the Boltzmann constant, and T is substrate temperature. Amounts of the bonded H in films, however, decreased with an increase in the substrate temperature as confirmed by the present work and other reports.[15, 16] Thus, the possibility of a reduction of the stress-relaxation effect caused by homogeneously distributed H can be promoted at excessively high substrate temperatures. In Fig. 1, although the films included almost the same amounts of Ar, the large difference of the film stresses is shown [between (○) and (▲)]. This is probably due to the variation in the degree of the distortions; these distortions are caused by the deviation of the bond angle and the difference of H-distribution in the films, which are affected by substrate temperature changes.

V. CONCLUSIONS

The relation between the stresses of the sputtered Si : H films and the film deposition conditions was investigated. Further the film composition and the deviations of Si bond angle were measured. From these results, it was confirmed that the sputtered Si : H film stresses are affected by the amounts of Ar included in the films. The structural disorders, such as deviation of Si bond angle, also affect the film stresses. On the other hand, homogeneous distribution of the bonded H in the films contributed to the reduction of Si : H film stresses. The extent that these factors contribute to film stresses can be influenced by changing the substrate temperatures.

ACKNOWLEDGMENTS

The authors would like to acknowledge Dr. A. Matsuda and T. Sasaki of the Electrotechnical Laboratories in Tsukuba for CPM and M. Fujishima of MST for Raman measurements.

REFERENCES

1. S. Kawakami, 9th Optical Sensors Conference (Firenze, Italy), paper Th2 (May 1993), Vol. 12.
2. S. Kawakami and O. Hanaizurni, Trans. Institute of Electronics, Information and Communication Engineers (IEICE), C-I **77**, 334 (1994).
3. K. Siraishi and S. Kawakami, Opt. Lett. **15**, 516 (1990).
4. L. M. Mack and A. Reisman, J. Electrochem. Soc. **136**, 3433 (1989).
5. W. Beyer, *Tetrahedrally Bonded Amorphous Semiconductors*, edited by D. Adler and H. Fritzshce (Plenum Press, New York, 1985), p. 129.
6. G. Ganguly and A. Matsuda, Phys. Rev. B **7**, 3661 (1993).
7. J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, and M. I. Nathan, Phys. Rev. Lett. **26**, 642 (1971).
8. M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).
9. D. Beeman and R. Albert, Adv. Phys. **26**, 339 (1977).
10. M. F. Thorpe, Phys. Rev. B **8**, 5352 (1973).
11. H. Takahashi, H. Nagata, and H. Kataoka, unpublished.
12. J. A. Aboaf, J. Electrochem. Soc. **116**, 1732 (1969).
13. S. R. Kurtz, Y. S. Tsuno, and R. Tsu, Appl. Phys. Lett. **49**, 951 (1986).
14. J. A. Thoronton, J. Tabock, and D. W. Hoffman, Thin Solid Films **45**, 387 (1977).
15. C. T. Wu, Thin Solid Films **64**, 103 (1979).
16. H. Takahashi, H. Nagata, and H. Kataoka, Jpn. J. Appl. Phys. **33**, 4978 (1994).
17. R. S. Nowicki, W. D. Buckley, W. D. Mackintosh, and I. V. Mitchell, J. Vac. Sci. Technol. **11**, 675 (1974).
18. J. P. Harbison, A. J. Williams, and D. V. Lang, J. Appl. Phys. **55**, 946 (1984).
19. J. C. G. de Sacde, C. N. Afonso, J. L. Escudero, R. Serna, F. Catalina, and E. Bernabeu, Appl. Opt. **31**, 6133 (1992).
20. D. Beeman, R. Tsu, and M. F. Thorpe, Phys. Rev. B **32**, 874 (1985).

21. H. Takahashi, H. Nagata, H. Kataoka, and H. Takai, J. Appl. Phys. **75**, 2667 (1994).
22. J. C. Knights, Jpn. Appl. Phys. **18**, 101 (1979).
23. S. Iizima, H. Okushi, A. Matsuda, S. Yamasaki, K. Nakagawa, M. Mitsumura, and K. Tanaka, Jpn. J. Appl. Phys. **19**, 521 (1980).
24. J. R. Abelson, Appl. Phys. **A56**, 493 (1993).
25. R. Banerjee, S. N. Sharma, A. K. Bandyopadhyay, A. K. Batabyal, and A. K. Barua, J. Mater. Sci. Lett. **12**, 1316 (1993).
26. S. C. Moss and J. F. Graczyk, *Proc. 10th Int. Conf. Phys. Semicond.*, edited by S. P. Keller *et al.* (U.S. Atom. Energy Commission, 1970), p. 658.
27. K. Tsuji and S. Minomura, J. Phys. **42**, C4–233 (1981).
28. A. Barna, P. B. Barna, G. Radnoczi, L. Toth, and P. Thomas, Phys. Status Solidi A **41**, 81 (1977).
29. J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).
30. G. H. Dohler, R. Dandoloff, and H. Bilz, J. Non-Cryst. Solids **42**, 87 (1980).
31. T. Shimizu, J. Non-Cryst. Solids **59/60**, 117 (1983).