Second harmonic generation in hydrogenated amorphous silicon

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The first application of the second harmonic generation (SHG) technique to investigate the structure of *a*-Si:H films is reported. Dependence of SHG on the type of substrate material and the temperature during deposition has been observed. The origin of SHG is discussed. A stress model is proposed to explain the experimental results. It is suggested that the second harmonic is generated in a strained layer close to the substrate.

I. INTRODUCTION

The structure of disordered solids is an area of active investigation because it is instrumental in determining their physical properties. The case of amorphous Si (*a*-Si) is particularly interesting, since it is of considerable technological value, especially in its hydrogenated version. Also, because of its relative simplicity, *a*-Si is often taken as the prototype covalent glass. By gaining understanding of structural features of *a*-Si, one can hope to disentangle a little bit of the complex processes underlying the physics of disordered materials.

The nonlinear optics increasingly becomes an important investigation tool of materials because of its sensitivity to symmetry. The reason is that the nonlinear response is described by higher than rank 2 tensors. For systems with inversion symmetry the susceptibility $\chi^{(2)}$ is zero in dipole approximation and thus any observed $\chi^{(2)}$ must be generated in regions where this symmetry is broken. For example, in Si and thermal SiO_2, because of the bulk inversion symmetry, the main contribution to the second order nonlinearity stems from the surface and interface regions. In recent years much valuable information about Si-SiO_2 system has been gained from experiments on optical second-harmonic generation (SHG).[1–5]

In this paper observation of second-harmonic generation in *a*-Si:H thin film is presented. It is demonstrated that nonlinear optical response can be successfully applied for the study of amorphous materials and, in particular, to determine the symmetry properties of the *a*-Si. As far as we know, no such investigations have been reported so far.

II. EXPERIMENTAL

The experiments were performed on intrinsic *a*-Si:H films deposited by radio-frequency (13.56 MHz, 48 mW/cm^2) glow discharge in a capacitive reactor from a mixture of 10% SiH_4 and 90% hydrogen. The films, 125 nm thick, were deposited onto three different substrates, namely, fused quartz plates, Corning glass 7059, and soda-lime glass. The deposition was carried out at substrate temperatures of 150 and 240 °C. Earlier Raman studies from our laboratory[6] have shown that 1 μm thick *a*-Si:H films prepared at the same technological conditions exhibit amorphous matrix as demonstrated by the TO bond configuration.[7]

A YAG:Nd^{3+} laser ($\lambda = 1.064$ μm, pulse duration of 30 ns and pulse energy of 1 mJ) was used as a pumping source for SHG. The SH signal was detected by a photomultiplier and fed into a computer-controlled data acquisition system. The probe beam was polarized either parallel (*p*-polarization) or normal (*s*-polarization) to the plane of incidence. The SH intensity was measured as a function of the angle of incidence θ while the sample was rotated around an axis laying in the film plane.

The pump energy of 1.17 eV (1.064 μm) is substantially below the absorption edge of the *a*-Si:H of 1.8 eV.[7] The absorption, therefore, is due to transitions from tail states as indicated by spectroscopic study of amorphous hydrogenated *a*-Si:H films[8] and is essentially low. Nonetheless, the laser beam on the film surface was defocused to a spot with a diameter of about 3 mm to decrease the intensity in order to avoid structural changes.

III. RESULTS AND DISCUSSION

Measurements of the SHG by the film were taken for both *p*- and *s*-polarized pump and *p*- and *s*-positions of the SH-radiation analyzer. In the films deposited on fused quartz substrates the SHG signals were at the noise level at any polarization of the pump and position of the SH-radiation analyzer. In all other cases only *p*-polarized SH radiation I_p under a *p*-polarized pump was observed. Zero SHG signal from the samples on fused quartz substrates seems surprising in comparison to relatively high signal from ones on glass substrates. This item will be discussed below.

The absence of *s*-polarized SH radiation suggests that the films have a reflection symmetry about a plane containing the normal to the film. The observed variation of the I_p, as the sample is rotated changing θ, is governed by the structural symmetry of the film. In Figs. 1 and 2 SH signals I_p are displayed. The symmetry around $\theta = 0$ implies that the films are optically homogeneous at dimensions of at least the light beam spot of 3 mm.[9] The $I_p = 0$ at $\theta = 0$ indicates no isotropic background signal, i.e., there are no polar directions lying in the plane of the film and the film behaves as an azimuthally isotropic media. Thus the symmetric pattern of the I_p as a function of rotation is indicative of ∞m symmetry group of the films. This is a symmetry group meaning a mirror sym-

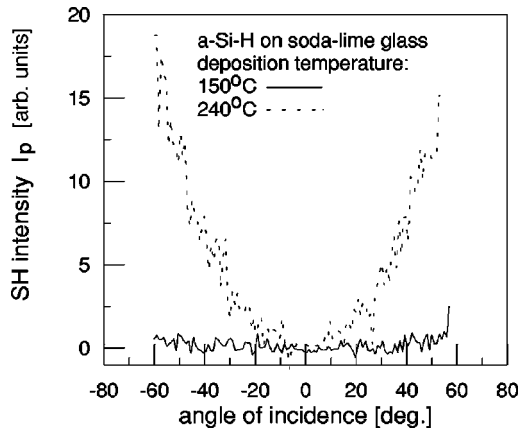

FIG. 1. SH intensity I_p as a function of the angle of incidence under *p*-polarized pump of *a*-Si:H films on soda lime-glass substrate at film deposition temperatures of 150 and 240 °C.

metry with a polar axis of order ∞ perpendicular to the plane of the film. This latter is relevant to the state of the amorphous Si:H films deposited on a substrate. It can be seen in Figs. 1 and 2 that the I_p depend on substrates and their temperature during film deposition. The films exhibit higher I_p at the higher substrate temperature for both substrates.

The crystalline Si generates no significant SHG response because of the inversion symmetry of the bulk. It has been shown that in dipole approximation the SHG is forbidden and the SH signal comes from the surface dipole and bulk quadrupole contributions.[10] The *a*-Si, as an amorphous material, also does not generate SH. In our results an analogy can be seen with the surface of the crystalline Si or its interface with other layers,[1–5,11–13] where the inversion symmetry is lifted out. The observation of a polar axis perpendicular to the plane of the *a*-Si:H film arises because of the breaking of the inversion symmetry at the surface and the interface to the substrate.

The absence of Maker fringes in SHG pattern in Figs. 1 and 2 indicates that SH contribution from the glass substrate is small, and does not exceed the noise level. Thus the SHG source in our experiments is amorphous silicon film subjected to polar effect of substrate surface. Whereas the film is transparent for the pump radiation, significant absorbance at SH wavelength takes place, resulting in resonance increase of respective nonlinearities.

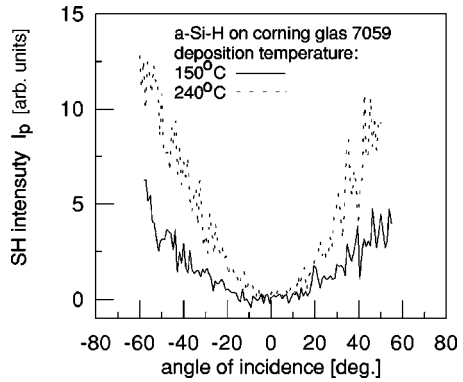

FIG. 2. SH intensity I_p as a function of the angle of incidence under *p*-polarized pump of *a*-Si:H films on Corning glass 7059 substrate at film deposition temperatures of 150 and 240 °C.

TABLE I. Thermal expansion coefficients α_s and thermal stress σ_{th} for the different substrates and deposition temperatures.

Substrate	$\alpha_s \times 10^{-6}/°C$	$\sigma_{\text{th}} \times 10^6$ Pa at 150 °C	$\sigma_{\text{th}} \times 10^6$ Pa at 240 °C
Soda-lime glass	8.36	225	380
Corning glass 7059	4.6	119	201
Fused quartz	0.52	3.4	5.7

We assume that the possible origin of the abovementioned polar effect is a transitional strained layer of the *a*-Si-H film close to the substrate. This suggestion allows us to account for the observed SHG dependence on substrate type and film deposition temperature, and characterize this layer as the main source of SHG. It should be noted that, similarly to our results, SHG was observed from the strained layer at the interface in crystalline Si-SiO_2 structures.[14,15]

The stress in *a*-Si:H has often been discussed in relation to the electronic properties of the films.[16,17] Our experiments show that the higher total stress at higher deposition temperature correlates with the enhanced polar effect.

The total mechanical stress consists of intrinsic and thermal components. The intrinsic stress appears during the deposition and is related to the structure of the film. The thermal stress appears after deposition when cooling down the films to room temperature due to the difference in thermal expansion coefficients of the two solids.

The thermal stress σ_{th} can be estimated from the well-known relationship

$$\sigma_{\text{th}} = (\alpha_s - \alpha_f)(T - T_d)E/(1-\nu),$$

where α_s and α_f, are the coefficients of thermal expansion of the substrate and the film, respectively, T is the room temperature and T_d is temperature of the film deposition, and E is the Young's modulus and ν is Poison's ratio of the film. The values of E and ν are assumed to be 1.7×10^{11} Pa and 0.22, respectively.[17] The coefficients α_s and the calculated stress σ_{th} are given in Table I. It can be seen that α_s, and hence the stress σ_{th}, for the three substrates differ significantly. The higher film stress, either due to higher α_s or higher deposition temperature, could account for the higher SHG signal I_p as demonstrated in Figs. 1 and 2. The zero SH signal from films on fused quartz substrate could be due to the extremely low value of σ_{th} for these samples.

The data analysis on the basis of a simple thermal stress model, presented above, can account for the overall dependence of the SHG on preparation conditions. However, in order to get a more detailed insight into the polar behavior of the films we have to take into account the intrinsic stress that appears during deposition and is related to the structure of the film.[17–19] The intrinsic stress is due to the local strain of the Si-Si bonds in the bulk of the material as well as the film-substrate mismatch strain.

The local strain caused by bond-angle and stretch-bond fluctuations of the bulk depends mainly on the deposition conditions. The substrate temperature during deposition has implications on the structural properties as well as on the hydrogen content of the film. Low-temperature films incorporate more structural defects, such as dangling bonds and

voids, the stress being relaxed by the less dense structure. Moreover, because of the higher hydrogen content, highly strained Si-Si bonds are eliminated by H interstitial mechanism.[7,20] The films grown at higher substrate temperature are more dense with less hydrogen incorporated, which results in more stressed films and, consequently, is consistent with the observed increase in the SHG intensity in Figs. 1 and 2.

Obviously, the intrinsic structural stress as well as the thermal stress, as discussed above, can have similar implications on the polar behavior of the films. In the case of soda-lime glass substrates another origin enhancing additionally the polar effect can be the thermal diffusion of alkaline atoms from glass substrates into the transitional layer.[21]

In summary, a SHG nonlinear response was observed in *a*-Si:H films. Angle- and polarization-dependent SHG measurements showed that the films have a ∞m symmetry, are polar perpendicular to the surface, and hence second harmonic active. It has been shown that SHG is sensitive to deposition parameters, the source of SHG response being the strained region near the substrate. As already shown in the case of crystalline materials, SHG has a potential as a nondestructive tool for structural probing of noncrystalline thin films.

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[1] G. Lübke, D. J. Bottomley, and H. M. van Driel, Phys. Rev. B **47**, 10 389 (1993).
[2] W. Daum, K.-J. Krause, U. Reichel, and I. Ibach, Phys. Rev. Lett. **71**, 1234 (1993).
[3] C. Ohloff, C. Meyer, G. Lübke, T. Löffler, T. Pfeifer, H. G. Roskos, and H. Kurz, Appl. Phys. Lett. **68**, 1699 (1996).
[4] C. Ohloff, G. Lübke, C. Meyer, and H. Kurz, Phys. Rev. B **55**, 4596 (1997).
[5] S. V. Govorkov, V. I. Emel'anov, N. I. Koroteev, G. I. Petrov, I. L. Shumay, and V. V. Yakovlev, J. Opt. Soc. Am. B **6**, 1117 (1989).
[6] P. Danesh, I. Savatinova, and A. Szekeres, Proc. SPIE **983**, 1078 (1993).
[7] S. R. Elliot, Adv. Phys. **38**, 1 (1989).
[8] A. Esser, H. Hessel, H. Kurz, C. Wang, G. N. Parsons, and G. Lucovsky, J. Appl. Phys. **73**, 1235 (1993).
[9] I. A. Maslyanitsyn, V. D. Shigorin, and S. G. Yudin, Quantum Electron. **27**, 437 (1997).
[10] O. A. Aktsipetrov, I. M. Baranova, and Yu. A. Ilinskii, Sov. Phys. JETP **64**, 167 (1986).
[11] W. Daum, K.-J. Krause, U. Reichel, and I. Ibach, Phys. Rev. Lett. **71**, 1234 (1993).
[12] C. Ohloff, C. Meyer, G. Lübke, T. Löffler, T. Pfeifer, H. G. Roskos, and H. Kurz, Appl. Phys. Lett. **68**, 1699 (1996).
[13] T. F. Heinz, F. J. Himsel, E. Palange, and E. Burstein, Phys. Rev. Lett. **63**, 644 (1989).
[14] V. V. Savkin, A. A. Fedyanin, F. A. Pudonin, A. N. Rubtsov, and O. A. Aktsipetrov, Thin Solid Films **336**, 350 (1998).
[15] C. Meyer, G. Lübke, Z. G. Lü, A. Gölz, and H. Kurz, J. Vac. Sci. Technol. B **14**, 3107 (1996).
[16] W. E. Spear and M. Heintze, Philos. Mag. B **54**, 343 (1986).
[17] K. S. Stevens and N. M. Johnson, J. Appl. Phys. **71**, 2628 (1992).
[18] S. Guo and W. Wang, Thin Solid Films **219**, 135 (1992).
[19] Y. Kitsuno, G. Cho, J. Drewery, W. Hong, and V. Perez-Mendez, Jpn. J. Appl. Phys. **33**, 1261 (1994).
[20] R. Tsu, Sol. Cells **21**, 19 (1987).
[21] D. Nesheva and P. Danesh, Philos. Mag. B **63**, 1139 (1991).