Spectroscopic second harmonic generation measured on plasma-deposited hydrogenated amorphous silicon thin films

Spectroscopic second harmonic generation measured on plasma-deposited hydrogenated amorphous silicon thin films

W. M. M. Kessels,[a] J. J. H. Gielis, I. M. P. Aarts,
C. M. Leewis, and M. C. M. van de Sanden
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 6 April 2004; accepted 14 September 2004)

Optical second harmonic generation (SHG) has been measured for plasma-deposited thin films of hydrogenated amorphous silicon (*a*-Si:H) at different polarization states for pump photon energies between 1.0 and 1.7 eV. Distinct resonance peaks are observed in this energy range and it is shown that the SH signal originates from an isotropic contribution at both the film-surface and substrate-interface region. The possibility that the SH signal originates from surface and interface dangling bond states of *a*-Si:H is discussed. © *2004 American Institute of Physics*.
[DOI: 10.1063/1.1812836]

The widespread application of (plasma-enhanced) chemical vapor deposited thin films in optoelectronic devices makes the understanding of their electronic performance a major effort in materials research. For films such as amorphous silicon (*a*-Si:H), silicon nitride (*a*-SiN_x:H), and silicon oxide (*a*-SiO_x), the electronic properties are for a large part determined by their defects states. Especially surface and interface defects play an important role in this respect because device operation is generally significantly affected by the interface properties while at the same time the importance of these surface and interface defects is growing due to the shrinking device dimensions.

The investigation of deposited thin films by nonlinear optical techniques such as second harmonic generation (SHG)[1] is very interesting in this respect. The SHG technique is noninvasive and highly surface sensitive (for centrosymmetric media such as crystalline silicon and *a*-Si:H) and can therefore give spectroscopic information on the surface and interface properties of thin films while it can even be applied *in situ* during device fabrication. As a consequence, SHG has been very important in the investigation of crystalline silicon (*c*-Si) interface properties and especially the fact that SHG is sensitive for surface dangling bonds[2,3] and strained bonds[4] has led to full exploitation of the technique in *c*-Si surface science. SHG has also been applied extensively in the study of the technologically very relevant Si/SiO_2 interface as obtained from thermal or plasma oxidation of Si wafers.[5] In contrast, the application of SHG on plasma deposited films has not been explored yet, except for the recent studies on *a*-SiN_x:H microcavities by Lettieri *et al.*[6] and on *a*-Si:H thin films by Alexandrova, Danesh, and Maslyanitsyn.[7,8] In these studies the SH signal was not rigorously characterized while for the *a*-Si:H films no spectral dependence of the SH signal was investigated. In this letter, the SH response of thin *a*-Si:H films is investigated in detail addressing the polarization dependence, angle of incidence, and rotational isotropy of the SH signal. The spectral dependence is investigated to obtain more insight into the microscopic origin of the SH signal and its relation with surface dangling bond states is discussed.

The experiments have been carried out within the wavelength range 740–1200 nm (1.0–1.7 eV) using the idler beam of an optical parametric oscillator pumped by a frequency-tripled, *Q*-switched Nd:yttrium–aluminum–garnet laser with a 6 ns pulse duration and 30 Hz repetition rate. The laser energy has been set by a combination of a half wave retardation plate and a polarizer, while the polarization of the pump beam could be rotated by another half wave retardation plate. The polarization of the SH signal has been investigated by a polarizer in the SH detection channel which consists of a lens, monochromator, and photomultiplier. Absorptive filters have been used to eliminate any incident light at the second harmonic frequency in the pump beam and to block the pump radiation in the SH detection channel. Furthermore, the spectral sensitivity of the detection channel has been taken into account while a reference channel probing the SH signal from a GaAs substrate has been used to monitor the stability of the pump radiation. The wavelength of the pump radiation has been checked independently by a calibrated monochromator leading to an accuracy in pump photon energy of ±0.003 eV.

The *a*-Si:H films with a thickness of 9 and 1031 nm have been deposited by a rf plasma at a substrate temperature of 250 °C and with a deposition rate of 0.22 nm/s. Fused silica substrates have been used and it has been verified that the substrates did not produce a detectable level of SH radiation. The samples have been positioned on a substrate holder that can be rotated around the axis normal to the substrate. The experiments have been carried out at an angle of incidence of 45° while in a few cases the SH signal at normal incidence has also been investigated. The laser fluence on the sample has been kept constant at $\sim 100\ mJ/cm^2$ per pulse which is below the threshold for crystallization of the *a*-Si:H and no influence of the laser on the films has been observed. The data in this letter are presented in terms of the second-order nonlinear susceptibility $\chi^{(2)}$ (in arbitrary units) which is calculated from the square root of the SH signal. Furthermore, we have determined the thickness of the films and their linear optical properties in the range 0.7–5.0 eV by transmission-reflection spectroscopy.

[a]Author to whom correspondence should be addressed; electronic mail: w.m.m.kessels@tue.nl

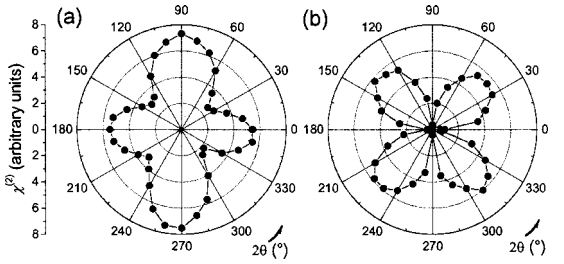

FIG. 1. Polar plot of $\chi^{(2)}$ for (a) *p*-polarized and (b) *s*-polarized SH signals from the 9-nm-thick *a*-Si:H film as a function of the input polarization of the pump radiation with a photon energy of 1.17 eV. The sample has been probed from the film-surface side of the sample at an incident angle of 45°. The half wave plate position of $2\theta=0°$ and 180° (90° and 270°) corresponds to a *s*- (*p*-)polarized pump beam.

A signal has been detected only at twice the photon energy of the pump radiation for both the films investigated, although this SH signal in terms of $\chi^{(2)}$ is a factor of ~25 higher for the 9-nm-thick film than for the 1031-nm-thick film at a photon energy of 1.17 eV. The fact that the SH signal does not increase with film thickness is in line with the expectation that the SH signal originates from the surface without a significant contribution from the *a*-Si:H bulk. The polarization dependence of the SH signal has been analyzed for an angle of incidence of 45°. Figure 1 shows $\chi^{(2)}$ for the *p* and *s* SH polarization state as a function of the polarization state of the pump beam at a photon energy of 1.17 eV for the 9-nm-thick *a*-Si:H film. The figure reveals (local) maxima for the *p*-*p*, *s*-*p*, and *mix*-*s* polarization configurations (with *s*-*p* denoting a *s*-polarized pump beam and *p*-polarized SH radiation, etc., and *mix* denoting a combination of *p* and *s* polarized pump radiation with both components equal in magnitude). For the *s*-*s* and *p*-*s* configuration no SH signal is observed above the noise level. This polarization dependence corresponds to a $\chi^{(2)}$ tensor that has only five nonvanishing tensor elements, i.e., $\chi^{(2)}_{xxz}=\chi^{(2)}_{yyz}$, $\chi^{(2)}_{zxx}=\chi^{(2)}_{zyy}$, and $\chi^{(2)}_{zzz}$ with *z* corresponding to the normal direction and *x* and *y* to the directions in the plane of the film. Rotation of the sample around its surface normal did not show a variation of the SH signal while no SH radiation has been detected for normal incidence of the pump beam. This reveals that the $\chi^{(2)}$ tensor corresponds to an isotropic surface described by ∞m symmetry[1] for the *a*-Si:H film.

Our observation of an isotropic surface described by ∞m symmetry is in agreement with the SHG study on *a*-SiN_x:H by Letteiri *et al.* They observed SH radiation for the *p*-*p* and *s*-*p* configuration and found the same input polarization dependence for the *s*-polarized SH radiation as shown in Fig. 1(b).[6] Our results are probably also in agreement with the results on *a*-Si:H films reported by Alexandrova and co-workers. They restricted their investigation to *p*-polarized SH radiation generated by *s*- and *p*-polarized pump radiation and they observed only a detectable level of SH radiation in the *p*-*p* configuration.[7] This can possibly be attributed to insufficient sensitivity of their setup for the much lower signal in the *s*-*p* configuration. We expect therefore that these observations for *a*-SiN_x:H and *a*-Si:H films indicate the same ∞m-symmetry class corresponding with an isotropic surface. This implies that the dipoles that lead to SH radiation are isotropically distributed on the surface but not directed perpendicularly to the plane of the film.[9]

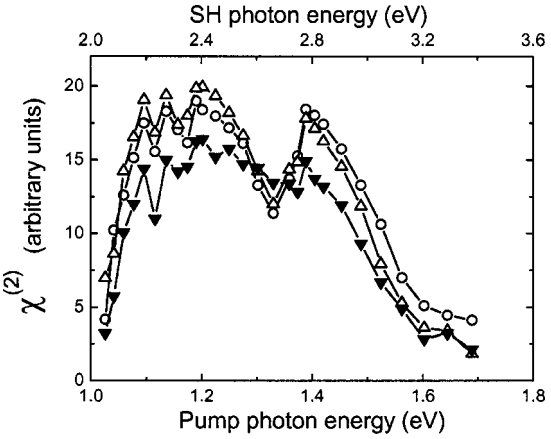

FIG. 2. $\chi^{(2)}$ of the 9-nm-thick *a*-Si:H film probed from the film-surface side as a function of the pump photon energy and the corresponding SH photon energy. Data are given for the polarization configurations *p*-*p* (△), *s*-*p* (○) and *mix*-*s* (▼) for an angle of incidence of 45°.

Probing the *a*-Si:H film through the fused silica substrate from the substrate-interface side has revealed similar results for the polarization dependence as well as for the experiment at normal incidence and the rotation about the film surface normal. Furthermore, for the 1031-nm-thick *a*-Si:H film similar observations were made although less clear due to a significantly lower SH signal. This lower signal for the thicker film can (partly) be attributed to interference effects in the *a*-Si:H film.[5] The fact that a SH signal is observed when probing from the film-surface and substrate-interface side reveals that the SH radiation is produced in both the film-surface and substrate-interface region of the films because the SH radiation, in contrast to the pump radiation, is effectively adsorbed when passing through the *a*-Si:H bulk. Therefore the SH radiation generated at the substrate interface has a reduced contribution to the SH signal when probing the *a*-Si:H from the film-surface side and vice versa and this contribution is basically zero in the case of the 1031-nm-thick film. To test whether the SH radiation is originating from the *a*-Si:H and not from the native oxide on the *a*-Si:H surface or from a silicon-oxide interface region, SHG experiments have also been carried out on an *a*-SiO_x film with a thickness of 80 nm as well as on a Si(100) substrate covered by a 2-nm-thick native oxide. No SH signal could be observed above the detection limit of the experimental setup used except for a very weak signal for the *a*-SiO_x film at *p*-*p* polarization configuration. We conclude therefore that the SH radiation from the films originates from the film-surface and substrate-interface region of the *a*-Si:H itself.

To obtain more insight into the microscopic origin of the SH response, spectroscopic scans of $\chi^{(2)}$ have been recorded for the 9-nm-thick *a*-Si:H film when probing the film from the film-surface side. The spectral dependence is shown in Fig. 2 for the *p*-*p*, *s*-*p*, and *mix*-*s* polarization configurations. At photon energies of 1.12, 1.22, and 1.26 eV it has been verified that the polarization dependence resembles the one given in Fig. 1. The spectral dependence is therefore roughly similar for all polarization configurations and clearly two maxima are observed in the spectra at a photon energy of ~1.2 and ~1.4 eV.

The resonance structure in the SH signal can either correspond to an optical transition that is resonant with the pho-

ton energy of the pump radiation or with the photon energy of the SH radiation. In the latter case, the transition would coincide with the highly probable linear optical transitions from the valence band to the conduction band of the *a*-Si:H. For *c*-Si such a kind of bulk transition is not observed by SHG except for the "distorted bulk" transition observed at 1.7 eV which corresponds to the 3.4 eV E_1 direct band gap transition in *c*-Si.[2–4] A resonance at the fundamental photon energy would, however, be in correspondence to observations for *c*-Si because SH radiation is resonantly generated between 0.9 and 1.6 eV by transitions involving surface dangling bond states of the *c*-Si. For example, Höfer has reported a featureless SH signal due to dangling bonds on a clean Si(100) and Si(111)-(7×7) surface[3] while Pedersen and Morgen could distinguish a resonance structure around $\sim$1.3 eV due to dangling bonds on a Si(111)-(7×7) surface.[2] Silicon dangling bonds also exist in *a*-Si:H films in which they are generally probed by techniques such as photothermal deflection spectroscopy in the same photon energy region.[10] The density of the dangling bonds is generally significantly enhanced in the surface and interface regions of the films,[11] although their overall density is generally much lower than for a clean *c*-Si surface due to passivation by hydrogen and the native oxide. Consequently, the fact that a SH signal is observed for *a*-Si:H in the same photon energy range as SH is generated on *c*-Si by surface dangling bonds suggests that the SH signal for *a*-Si:H is possibly also generated by dangling bonds.

Further comparison of the spectral dependence of the SH response in Fig. 2 with the observations of Pedersen and Morgen reveals that the SH resonance peak of *a*-Si:H shows some agreement with the resonance structure at $\sim$1.3 eV attributed to S_2-U_1 transitions.[2] The rough envelope of the resonance structures is quite similar apart from some possible differences in exact peak position and peak width. However, the presence of a second maximum in $\chi^{(2)}$ at $\sim$1.4 eV is different from the *c*-Si case while the *a*-Si:H data do not show a resonance around 1.7 eV as for *c*-Si. These differences in the spectral details can possibly be explained by differences in the local network structure of the *a*-Si:H and *c*-Si and the fact that a (roughly similar) resonance structure is observed in the photon energy range 1.0–1.6 eV suggests that the SH signal for *a*-Si:H is generated by Si dangling bonds. Moreover, for a SH signal arising from dangling bonds in the surface and interface region of the *a*-Si:H it is expected that it reflects an isotropic distribution described by the ∞m-symmetry class. The dangling bonds are isotropically distributed in the interface and surface region of the film which has a typical rms surface roughness of 0.26 nm as revealed by atomic force microscopy. In addition, also the observation that the SH signal generated by the *a*-Si:H is relatively low for the laser fluence used in this study is in agreement with the fact that most Si dangling bonds in the *a*-Si:H are passivated by hydrogen.

In summary, it is shown that the *a*-Si:H films exhibit a resonant SH response in the photon energy range 1.0–1.7 eV which originates from an isotropic contribution at both the film-surface and substrate-film side. On the basis of similarities with the spectral dependence of the SH response of clean *c*-Si substrates, it is discussed that the SH signal of the *a*-Si:H is possibly generated by Si dangling bonds states in the defect-rich surface and interface region. The potential of the SHG technique for surface- and interface-specific spectroscopy on *a*-Si:H thin films will be further explored by real time measurements during *a*-Si:H film growth.

This work has been supported by the Netherlands Foundation for Fundamental Research on Matter (FOM). The research of W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW). Professor Höfer of the Philipps-Universität Marburg is acknowledged for his help with setting up the SHG measurements.

[1] T. F. Heinz, in *Nonlinear Surface Electromagnetic Phenomena*, edited by H. Ponath and G. Stegeman (Elsevier, Amsterdam, 1991), p. 353.
[2] K. Pedersen and P. Morgen, Phys. Rev. B **52**, R2277 (1995).
[3] U. Höfer, Appl. Phys. A: Mater. Sci. Process. **63**, 533 (1995).
[4] W. Daum, H.-J. Krause, U. Reichel, and H. Ibach, Phys. Rev. Lett. **71**, 1234 (1993).
[5] G. Lüpke, Surf. Sci. Rep. **35**, 75 (1999).
[6] S. Lettieri, S. Di Finizio, P. Maddalena, V. Ballarini, and F. Giorgis, Appl. Phys. Lett. **81**, 4706 (2002).
[7] S. Alexandrova, P. Danesh, and I. A. Maslyanitsyn, Phys. Rev. B **61**, 11136 (2000).
[8] S. Alexandrova, P. Danesh, and I. A. Maslyanitsyn, Vacuum **69**, 391 (2003).
[9] The conclusion in Ref. 6 that the dipoles are isotropically distributed along the plane of the film but perpendicular to the film surface is in contradiction with the fact that a SH signal is observed for the *s-p* and *mix-s* polarization configurations.
[10] W. B. Jackson, N. M. Armer, A. C. Boccara, and D. Fournier, Appl. Opt. **20**, 1333 (1981).
[11] A. Asano and M. Stutzmann, J. Appl. Phys. **70**, 5025 (1991).