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Relation of the Si—H stretching frequency to the nanostructural Si—H bulk environment

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We propose a model which describes the frequency shift ($\Delta\omega_{SM}$) of the stretching mode (SM) of Si—H monohydrides (MH's) when incorporated in hydrogenated amorphous silicon (*a*-Si:H) with respect to the unscreened MH SM at $\sim 2099 \pm 2 \text{ cm}^{-1}$. The model is based on an effective medium approximation of the dielectric using multiple Lorentz-Lorenz dielectrics, corresponding to a host dielectric with MH's embedded in cavities, separately. The $\Delta\omega_{SM}$ as derived in this model correctly predicts all bulk MH-SM positions in *a*-Si:H films and relates it directly to the nanostructure of the MH bulk configurations.

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The frequency position of the stretching modes (SM's) of hydrides ($1970\text{--}2130 \text{ cm}^{-1}$) on well-defined oriented crystalline^{1,2} and amorphous silicon surfaces³ has been extensively studied with a satisfactory physical interpretation. Despite this, a detailed understanding of the frequency shift of the bulk SM's and the hydrogen incorporation configurations contributing to the bulk SM's is still lacking. It is well known that if hydrides (Si—H_x) are incorporated into the bulk of hydrogenated silicon (*a*-Si:H), the SM's broaden significantly and their frequency position shifts to lower values. Standard hydrogenated amorphous silicon (*a*-Si:H) has next to a broad high SM (HSM) at $2070\text{--}2100 \text{ cm}^{-1}$ a low SM (LSM) at ($1980\text{--}2010 \text{ cm}^{-1}$).⁴⁻⁹ Hydrogenated micro- or nanocrystalline silicon ($\mu\text{c-Si:H}$ or nc-Si:H , respectively) can have an additional small mode at $1895\text{--}1950 \text{ cm}^{-1}$,¹⁰⁻¹² an additional middle SM (MSM) around $2030\text{--}2040 \text{ cm}^{-1}$,¹⁰⁻¹³ and an additional HSM at $2100\text{--}2130 \text{ cm}^{-1}$.¹³ The exact assignment of these modes and the physical origin and interpretation of these modes have been a subject of many reports. One explanation of the difference between the LSM and HSM is that the origin is only the hydride type: monohydrides (MH's) contribute to the LSM and dihydrides (DH's) contribute to the HSM, whereas others claim that the distinction between LSM and HSM can be attributed to the hydride type and the bulk environment in which it resides.^{5,7-9} However, MH's can also contribute to the HSM, possibly when present on internal surfaces,^{7,9} and MH's at the so-called platelet surfaces are believed to be responsible for the observed MSM.¹⁰⁻¹³ The SM's at $1895\text{--}1950 \text{ cm}^{-1}$ possibly reflect a so-called bond centered hydrogen $\equiv\text{Si-H-Si}\equiv$,^{11,12} but a clear proof of this assignment is still lacking.

Recently, we were able to identify some important hydride bulk configurations in *a*-Si:H, such as the divacancy and the nanosized void configurations, using the relation between the film mass density and the hydrogen concentration.⁹ In this analysis, we used a multiple resonance Lorentz-Lorenz (LL) formalism, also known as the Clausius-Mossotti relation, for *a*-Si:H as proposed by Remes *et al.*¹⁴ Although this approach is very successful in describing the density of *a*-Si:H films, it fails to describe the physical origin of the frequency shift of the hydride stretching mode in *a*-Si:H, as we will show in this Brief Report.

In this Brief Report, we will derive the following expression for the frequency shift $\Delta\omega_{SM}$ of a MH which, as we will argue, depends explicitly on the nanostructural network environment (note that in this Brief Report the frequency ω is given in the unit cm^{-1} [$\omega(\text{cm}^{-1}) = 10^{-2}\omega(\text{s}^{-1})/(2\pi c)$], all other parameters are expressed in SI units):

$$\Delta\omega_{SM} = -\frac{10^{-4}}{24\pi^2 c^2 m \omega_0 \epsilon_0} \frac{K q_e^2}{V_{\text{Si}}} \quad (1)$$

In Eq. (1), m is the mass of the Si—H dipole, ω_0 is the MH eigenmode frequency without any dielectric screening, and c is the velocity of light. The effective screened charge q_e is related to the unscreened charge q_0 through Ω describing the screening of the effective charge of the electric force $F = -q_e E_{loc} = -q_0 \Omega E_{loc}$, with E_{loc} the Lorentz local field. In Eq. (1), K is a nanostructural parameter reflecting the averaged number of MH's per unit volume V_{Si} ($\sim 2 \times 10^{-29} \text{ m}^3$) of a Si atom in the *a*-Si:H network. A key message of this Brief Report is that we will demonstrate that Eq. (1) can explain the bulk MH frequency positions in *a*-Si:H. Moreover, we will argue that these positions are the result of the nanostructural incorporation configurations of MH's in *a*-Si:H. Although we discuss here the frequency shift for the particular case of *a*-Si:H, we expect that the treatment can be generalized to other covalent amorphous films containing hydrogen such as *a*-SiC:H, *a*-SiN_x:H, etc.

The eigenfrequency ω_0 of a freely vibrating $\text{Si}_3\equiv\text{SiH}$ dipole has been determined by Cardona⁴ by the linear extrapolation of the A_1 SM's of SiH_4 , Si-SiH_3 , and $\text{Si}_2\equiv\text{SiH}_2$ obtained from silane and polysilane molecules. This procedure gives $\omega_0 = 2099 \pm 2 \text{ cm}^{-1}$ and is in perfect agreement with the upper limit for MH frequency on *c*-Si and *a*-Si:H surfaces.¹⁻³ In addition, Cardona proposed that the shift of the SM ($\Delta\omega_{SM}$) of a hydride in the *a*-Si:H bulk is determined by the volume V of the cavity in which the Si—H dipole resides:⁴

$$\Delta\omega_{SM} = -\frac{10^{-4}}{24\pi^2 c^2 m \omega_0 \epsilon_0} \frac{3q_e^2}{V} \frac{\epsilon - 1}{2\epsilon + 1}, \quad (2)$$

with ϵ the dielectric of the surrounding medium. To the best of our knowledge, the derivation of Eq. (2) has never been reported in literature. Despite this, Eq. (2) has two important

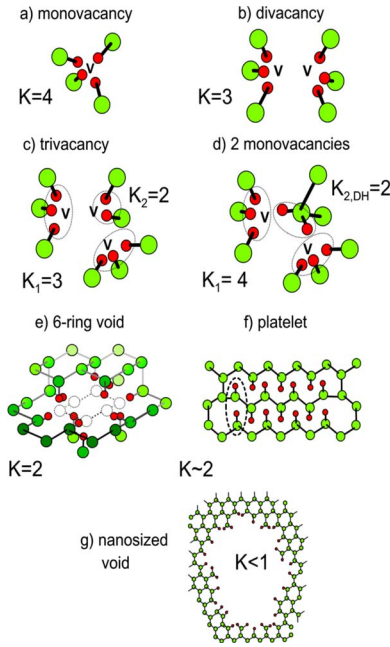


FIG. 1. (Color online) Overview of the configurations of hydride incorporation into Si bulk host with corresponding nanostructure parameter K as defined in the text.

shortcomings in order to explain the observed stretching mode frequencies in a -Si:H. First, Eq. (2) violates the LL dielectric approximation for a -Si:H as we will discuss below. Second, Eq. (2) describes one single MH in an empty cavity and therefore cannot describe a MH dipole density in a cavity which reflects the so-called cavity configurations (see Fig. 1) as determined unambiguously from the analysis based on the multiple resonance LL (Clausius-Mossotti) equation.⁹

Before we proceed by arguing the correctness of Eq. (1), we will briefly repeat our previous analysis of the a -Si:H density in which we considered a multiple LL dielectric model consisting of two types of oscillating dipoles, Si—Si ($j=1$) and Si—H ($j=2$) bonds.^{9,14} The multiple resonance LL (Clausius-Mossotti) equation based on harmonic oscillators for a homogeneous isotropic dielectric with dielectric constant ϵ is equal to

$$\sum_{j=1,2} N_j \frac{10^{-4} q_{j,e}^2}{4\pi^2 c^2 m_j \epsilon_0} \frac{1}{\omega^2 - \omega_{0,j}^2 + 4 \times 10^{-2} \pi i c \delta \omega} = 3 \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}, \quad (3)$$

with N_j the number density and $q_{j,e}$ the effective charge of mode j . The frequency shift of the eigenmode j which follows from Eq. (3) equals¹⁵

$$\Delta\omega_j \approx - \frac{10^{-4}}{24\pi^2 c^2 m_j \omega_{0,j} \epsilon_0} N_j q_{j,e}^2. \quad (4)$$

Note that Eq. (4) has a similar structure as the expression proposed by Cardona.⁴ Therefore, we anticipate that Cardona, to arrive at his expression [Eq. (2)], originally assumed that N_j is proportional to a uniformly distributed hydride density which would lead to an inverse dependence of $\Delta\omega_{SM}$

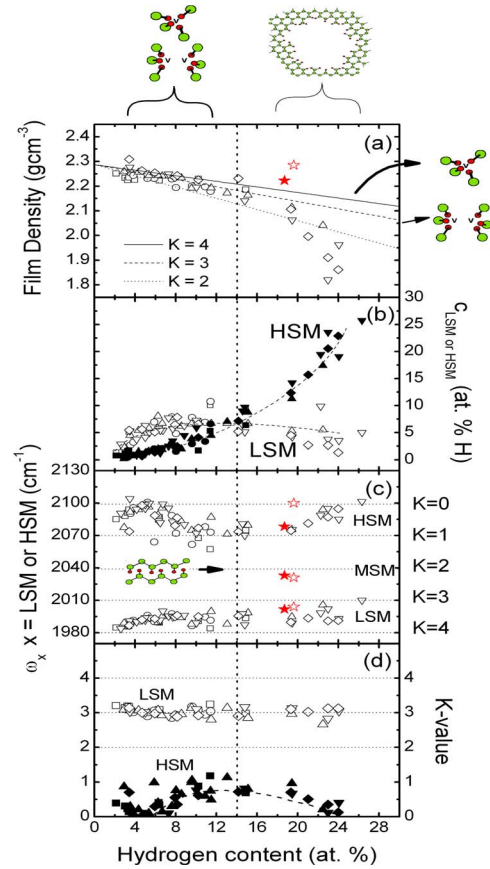


FIG. 2. (a) (Color online) The film mass density versus the hydrogen concentration c_H . The lines show the film mass density dependence on c_H for monovacancy (solid), divacancy (dashed line), and six-ring void (dotted line) as described in Ref. 9. (b) The hydrogen concentration, contributing to the LSM and HSM, versus c_H . The lines are guides for the eye. (c) The SM frequency position of the HSM and LSM versus c_H . (d) The nanostructure parameter K for the LSM and HSM using Eq. (1) and the Silsbee screening versus c_H . All data points represent a -Si:H films, except for the stars, which represent Si:H having also a MSM and is deposited in remote-plasma/rf-substrate-biased/ground-mesh configuration (solid, unpublished data) and from Ref. 10 (open).

on the cavity volume V in which one single hydride resides. In addition, Eq. (4) predicts that to first order, the frequency shift increases with increasing Si—H density. This is in clear disagreement with observations, i.e., with increasing LSM and hydrogen density, the frequency shift decreases [see, e.g., Fig. 2(c) and Ref. 9. In other words, although Eq. (3) can be used to give an adequate description of the a -Si:H density as shown previously, it fails in the description of the frequency shift of the hydrides.⁹ So, we arrive at the important conclusion that the hydrides in a -Si:H cannot be considered as single dipoles residing in a cavity which is embedded in a uniform dielectric medium.

To overcome these inconsistencies, we propose an alternative approach. The basic assumption is that, apart from the dielectric function of the host dielectric ϵ , which only depends on the amorphous Si—Si network, dielectric functions $\epsilon_{cav,i}$ for the i th cavity configuration type in which the k_i MH dipole types reside are introduced. Since the typical size of

TABLE I. The screening term Ω ($\varepsilon=3.5^2$) and the unscreened effective charge q_0 as deduced from the oscillator strength [Eq. (7)] and the frequency shift [Eq. (1)], respectively, for four different screening approaches: (A) no screening, (B) Smakula's homogeneous medium approach (Ref. 18), (C) Silsbee's approach of cavity induced screening (Ref. 19), and (D) the case for SiH₄ molecule (Ref. 20) as described in the text.

Screening approach	Ω	$q_{0,MH}$ (A_{LSM})(e)	$q_{0,MH}$ ($\Delta\omega_{SM}$) (e)
(A) No screening in bulk	1	0.40±0.02	0.39±0.01
(B) Dipoles in homogeneous dielectric	$(\langle\varepsilon\rangle+2)/3$	0.086±0.008	0.083±0.004
(C) Dipoles in cavity	$3\langle\varepsilon\rangle/(2\langle\varepsilon\rangle+1)$	0.28±0.02	0.27±0.01
(D) A ₂ SM of SiH ₄ molecule	1	0.28	

all vacancies present is much smaller than the relevant IR wavelengths, the bulk is described by a homogeneous effective dielectric function $\langle\varepsilon\rangle$, which is related to ε and $\varepsilon_{cav,k}$ through an effective medium approximation (EMA), e.g., the Bruggeman EMA:¹⁶

$$0 = \sum_i f_{cav,i} \frac{\varepsilon_{cav,i}(k_i) - \langle\varepsilon\rangle}{\varepsilon_{cav,i}(k_i) + 2\langle\varepsilon\rangle} + \left(1 - \sum_i f_{cav,i}\right) \frac{\varepsilon - \langle\varepsilon\rangle}{\varepsilon + 2\langle\varepsilon\rangle}. \quad (5)$$

In Eq. (5), $f_{cav,i}$ is the cavity volume fraction of the i th cavity configuration. For the LSM, $k_i=1$ and $\varepsilon_{cav,i}$ is described by a single resonance LL approximation similar to Eq. (3):

$$N_{cav,i} \frac{10^{-4} q_e^2}{4\pi^2 c^2 m_H \varepsilon_0} \frac{1}{\omega^2 - \omega_0^2 + 4 \times 10^{-2} \pi i c \delta \omega} = 3 \frac{\varepsilon_{cav,i}(\omega) - 1}{\varepsilon_{cav,i}(\omega) + 2}, \quad (6)$$

in which $N_{cav,i}$ is the local dipole density in the cavity equal to K/V_{Si} and K the nanostructural factor as defined earlier. The frequency shift $\Delta\omega_{SM}$ (which depends thus on K) of the dipole modes in the cavity as deduced from Eq. (6) equals Eq. (1):

$$\Delta\omega_{SM} = - \frac{10^{-4}}{24\pi^2 c^2 m \omega_0 \varepsilon_0} \frac{K q_e^2}{V_{Si}}.$$

Note that by using a single resonance LL approximation ($k_i=1$), we implicitly assume that the dipoles within a cavity have a minimal influence on each other. This assumption might be corroborated by the frequency shifts observed for hydride modes on hydrogenated silicon surfaces, where the dipole-dipole interaction leads to shift in the 2–9 cm⁻¹ range,¹⁷ values much smaller than the frequency shifts we discuss here (up to 120 cm⁻¹). Note that in Eq. (1), the only unknown parameters for MH's are K and q_e , where q_e depends on the screening environment and therefore might be different for the different MH's. Below, we will discuss this in detail and propose an explicit form for the effective charge

as a function of the bulk's effective dielectric constant.

An important consequence of the presented approach is the fact that the MH configurations within the bulk determine $\Delta\omega_{SM}$ through the nanostructure parameter K . In Fig. 1, all compact configurations in which a MH (and some dihydrides) can be incorporated in a -Si:H are summarized.⁹ The local MH density, $N_{cav,k}$, of the cavity, expressed in the above-defined K value is also indicated.

Before we return to the discussion of the absolute value of the frequency shifts as obtained from Eq. (1) and the value of the effective charge, we briefly discuss the frequency shifts observed. In previous work, we have found that for films with a hydrogen concentration $c_H < 14 \pm 2$ at. % H, hydrogen is predominantly incorporated in divacancies with a frequency in the range of 1980–2010 cm⁻¹ [see Fig. 2; the dashed line in Fig. 2(a) is the theoretical divacancy ruled density dependence and according to Fig. 2(b) the SM of MH's in vacancies has to contribute dominantly to the LSM for $c_H < 14 \pm 2$ at. %]. For $c_H > 14 \pm 2$ at. %, hydrogen is dominantly incorporated at the surface of nanosized voids with a frequency in the range of 2070–2100 cm⁻¹, as argued in Ref. 9 by the clear scaling between the hydrogen concentration in the HSM c_{HSM} and the void fraction. Also included are the data points of an a -Si:H film (stars) which shows a MSM around 2035 cm⁻¹ [see Fig. 2(c)] in line with the MSM range observed by others.¹⁰

If we consider the upper and lower limits of the LSM, MSM, and HSM, it is remarkable that the limits of the modes can roughly be described by the shift $\Delta\omega \sim K \times 30$ cm⁻¹ with respect to the unscreened mode at 2099 cm⁻¹, i.e., $K=0$ represents the upper limit of the HSM (~ 2100 cm⁻¹), $K=1$ represents the lower limit of the HSM (~ 2070 cm⁻¹), $K=2$ represents roughly the position of the MSM (~ 2040 cm⁻¹), $K=3$ represents the upper limit of the LSM (2010 cm⁻¹), and $K=4$ represents the lower limit of the LSM (1980 cm⁻¹). The position of the frequencies follows approximately the relation $\Delta\omega_{SM} \sim K \times (30 \pm 2)$ cm⁻¹. If we take for the effective mass m the mass of a hydrogen atom, we can determine q_e^2 . Using the approximate relation, we get $q_e^2 = 0.16e^2$, with e the elementary charge in line with Ref. 7. If we consider the MH bulk configurations linked with the K values, all SM's observed experimentally can be predicted. $K=4$ and $K=3$ represent the monovacancy (~ 1980 cm⁻¹) and divacancy (~ 2010 cm⁻¹), respectively. This is in perfect agreement with the density analysis of Figs. 2(a) and 2(b) that hydrogen bonded to divacancies contributes to the LSM. Furthermore, the MSM, believed to be caused by MH vibrations of the platelet configuration,¹⁰ is reflected by $K \sim 2$. This K value reflects indeed the hydrogen in the platelet configurations as shown in Fig. 1. $K < 1$ ($\omega_{SM} > 2070$ cm⁻¹) reflects hydrogen bonded to a surface and is in excellent agreement with the HSM corresponding to hydrogen bonded to the nanosized void surface. Thus, Eq. (1) correctly predicts all MH SM's.

The presented approach to describe the frequency shift, Eq. (1), can be corroborated if the effective charge could be determined in an independent way. The effective screened charge can also be determined, using experimental data of the oscillator strength of the LSM, from the expression $N_{H,LSM} = A_{LSM} \int \omega^{-1} \alpha(\omega) d\omega$, where A_{LSM} is the so-called pro-

portionality constant. According to Smakula's relation, A_{LSM} equals¹⁸

$$A_{LSM} = \frac{4mc^2 \varepsilon_0 \langle \varepsilon \rangle^{1/2} \omega_0}{q_e^2} = \frac{4mc^2 \varepsilon_0 \langle \varepsilon \rangle^{1/2} \omega_0}{q_0^2 \Omega^2}. \quad (7)$$

Using the empirical value of $A_{LSM} = (9.1 \pm 1.0) \times 10^{19} \text{ cm}^{-1}$ (Ref. 9) and Eq. (7), we get $q_0^2 \Omega^2 = (0.17 \pm 0.02)e^2$, which is in excellent agreement with the value determined from the frequency shift [Eq. (1)] and in line with Refs. 7 and 8. Note that the $q_e^2 = q_0^2 \Omega^2$ term describes the averaged charge screening, i.e., for the typical configurations as depicted in Fig. 1, not every dipole will see the exact same local electric field due to its orientation. However, as it turns out, apparently the effective screened charge is not much affected by the nanostructural environment and can be described by a single value (i.e., $\sim 0.4e$). This result also implies that the oscillator strength does not depend too much on the different MH configurations, in agreement with earlier reports.⁷⁻⁹

The determination of the unscreened effective charge q_0 from the oscillator strength or the frequency shift of the bulk hydrides is not straightforward. In addition, the fact that the exact description of the screening approach is not known and the fact that the screening term Ω ($\langle \varepsilon \rangle$) will be a function of $\langle \varepsilon \rangle$, which varies from sample to sample, make the determination of q_0 even more challenging. Despite these difficulties, we summarize averaged q_0 values in Table I as obtained using screening models of dipoles reported in literature, i.e., no screening $\Omega=1$, screening due to a uniform dielectric [Lorentz screening $\Omega = (\langle \varepsilon \rangle + 2)/3$ (Ref. 18)], or screening in a spherical cavity [Silsbee, $\Omega = 3\langle \varepsilon \rangle / (2\langle \varepsilon \rangle + 1)$ (Ref. 19)]. The unscreened q_0 of a MH can be deduced alternatively from the A_2 symmetry mode at 2189 cm^{-1} of the SiH_4 molecule with $A_{\text{SiH}_4} = 4.3 \times 10^{19} \text{ cm}^{-1}$ (Ref. 20) value (or $\frac{1}{4} A_{\text{SiH}}$ per Si—H bond). We find $q_0 = 0.16\sqrt{3}e = 0.28e$ using Eq. (7) with $\Omega=1$, $\langle \varepsilon \rangle=1$, and the fact that $q_{0,MH \text{ in } DH(A_2)} = 1/\sqrt{3}q_{0,MH}$ (q_0 reflects in the A_2 symmetry the q_0 of a single MH as part of the DH A_2 vibration). The q_0 values obtained by screening approach C, reflecting dipoles in a spherical cavity, give values closest to the unscreened q_0 values of the molecular vibration mode. This observation implies that the

screening of a MH in the bulk is best described by approach C.

To test the effect of the variations in $\langle \varepsilon \rangle$ via the $\Delta\omega_{SM}$ data in Fig. 2(c), we have made the results independent of $\langle \varepsilon \rangle$. The nanostructural parameter K of the LSM is determined for the results, as shown in Fig. 2(c), using Eq. (1) with the experimentally obtained ω_{LSM} and $\varepsilon_{\omega \rightarrow \infty}$ (~ 7.0 – 13.0) values using $q_0 = 0.27e$ and $\Omega = 3\langle \varepsilon \rangle / (2\langle \varepsilon \rangle + 1)$. The K values of the LSM show a narrow distribution around $K \sim 3$ and are independent of the hydrogen content, supporting the correctness of the introduced analyses. The $K \sim 3$ reflects that MH's in divacancies are the dominant contributor to the LSM in line with the density analyses.⁹ The nanostructural K -value analysis provides even more detailed information on the MH bulk configuration than our previous results based on the density analysis using the Clausius-Mossotti relation.⁹

In Fig. 2(d), the K value of the HSM is also shown assuming that the contribution of MH's dominates the HSM. The HSM values have a $K < 1$, reflecting that hydrides at surfaces of nanosized voids contribute to the HSM and have a minimum around $c_H = 6 \text{ at. } \%$. As will be discussed in great detail in a future publication, this approach is not valid for the HSM for $c_H < 6 \text{ at. } \%$ ($i \neq 1$ and $k_i \neq 1$), as for very dense a -Si:H films a significant fraction of compact DH's [as depicted in Fig. 1(d)] will contribute to the small HSM absorption as well. For example, if we consider the same approach for the DH, we find a $K \sim 2$ for the HSM for very dense films. If we assume that the additional SM's in $\mu\text{c-Si:H}$ or nc-Si:H in the spectral range 1895 – 1950 cm^{-1} have roughly the same q_0 value, we find a K value around 5 – 7 . These typical values in the latter case would reflect a compact hydrogen incorporation configuration in line with the mode's assignment to the bond centered hydrogen as proposed by Agarwal *et al.*¹¹ and Fujiwara *et al.*¹²

Summarized, the postulated Eq. (1) links the frequency shift of the hydride SM's in the bulk with the hydride's nanostructural environment using only two parameters, K and q_0 . The obtained K value and q_0 value for the LSM are in agreement with the density analysis⁹ and independent oscillator strength measurements. The postulated model reveals that screening of the hydrides in the bulk is best described by the Silsbee approach.¹⁹

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¹Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. **53**, 282 (1984).

²V. A. Burrows *et al.*, Appl. Phys. Lett. **53**, 998 (1988).

³W. M. M. Kessels *et al.*, J. Vac. Sci. Technol. A **20**, 781 (2002).

⁴M. Cardona, Phys. Status Solidi B **118**, 463 (1983).

⁵M. H. Brodsky *et al.*, Phys. Rev. B **16**, 3556 (1977).

⁶A. A. Langford *et al.*, Phys. Rev. B **45**, 13367 (1992).

⁷W. Beyer and M. S. Abo Ghazala, MRS Symposia Proceedings No. 507 (Materials Research Society, Pittsburgh, 1998), p. 601.

⁸J. D. Ouwers and R. E. I. Schropp, Phys. Rev. B **54**, 17759 (1996).

⁹A. H. M. Smets *et al.*, Appl. Phys. Lett. **82**, 1547 (2003).

¹⁰S. Vignoli *et al.*, J. Non-Cryst. Solids **299-302**, 220 (2002).

¹¹S. Agarwal *et al.*, J. Vac. Sci. Technol. B **22**, 2719 (2004).

¹²H. Fujiwara *et al.*, Surf. Sci. **497**, 333 (2002).

¹³S. Lebib and P. Roca I Cabarrocas, J. Appl. Phys. **97**, 104334 (2005).

¹⁴Z. Remes *et al.*, Phys. Rev. B **56**, R12710 (1997).

¹⁵K. E. Oughstun and N. A. Cartwright, Opt. Express **11**, 1541 (2003); **11**, 2791 (2003).

¹⁶T. C. Choy, *Effective Medium Theory, Principles and Applications* (Oxford University Press, 1999).

¹⁷K. Kuhnke *et al.*, J. Chem. Phys. **100**, 6896 (1994).

¹⁸A. Smakula, Z. Phys. **59**, 603 (1930).

¹⁹R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

²⁰H. Wieder *et al.*, Phys. Status Solidi A **74**, 329 (1982).