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Effect of plasma parameters on the amorphous to microcrystalline silicon transition

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Abstract

A study of the role of the main plasma parameters on the transition from microcrystalline to amorphous silicon growth was performed, considering also the possibility to use plasma diagnostics for the prediction of this transition. Experimental measurements have shown that charged species do not play a significant role in the transition while Spatially Resolved Emission Spectroscopy was found to present a potential to be used as an in-situ diagnostic tool for the prediction of the transition. Calculations of the ion and hydrogen atom fluxes have shown that they both decrease in the transition region; however the hydrogen atoms flux was found to be about three orders of magnitude higher compared to the ion flux, implying a less important role of the later species in the transition. Possible scenarios concerning the energy transfer from hydrogen atoms and ions to the surface are presented and the limited case were ions can play a significant role on the deposition process is discussed.

Keywords: Microcrystalline silicon; Amorphous silicon; Growth transition; Optical emission

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) has drawn a lot of attention due to its successful applications in thin film solar cells. Recently, solar cells with rather high efficiencies were grown close to the μc-Si:H/a-Si:H transition, indicating that the structure phase mixture maybe important for the solar cells efficiency [1,2]. In addition, in these conditions μc-Si:H is deposited at relatively high rates, an absolutely necessary condition for making the production of microcrystalline silicon solar cells feasible. However, the determination of the SiH_4/H_2 process conditions that lead to the desired thin film structure is a difficult procedure that depends on almost all the macroscopic plasma parameters [3,4].

Taking this into account, the present work has two major goals: the first one is to investigate the μc-Si:H process at conditions near the transition from amorphous to microcrystalline growth in order to identify which of the deposition parameters have a critical role in this phase change. Based on the results of this investigation, the second goal is to determine which diagnostic tool and under which conditions can be applied for a fast and reliable determination of μc-Si:H deposition conditions on the onset of crystallinity.

Several diagnostics techniques together with calculations of the ion bombardment and hydrogen atoms fluxes were applied for the accomplishment of the first goal. More precisely, electrical measurements were used for the calculation of the plasma power and impedance while Spatially Resolved Optical Emission Spectroscopy (SROES) of electronically excited SiH* ($A^2\Delta$) and H_β radicals was applied for recording changes in the production and distribution of these species in the discharge space. Moreover, the deposition rate was measured in situ using Laser Reflectance Interferometry, while the crystallinity of the films was determined by Laser Raman Spectroscopy.

2. Experimental

The measurements were carried out in a capacitively coupled Ultra High Vacuum parallel plate reactor having a base vacuum of 10^{-9} mbar. In order to investigate in detail the phase change we chose to perform the experiments using a total working pressure of 333.3 Pa and a constant interelectrode gap (15 mm). As resulted in a previous work of this group, these conditions lead to an optimum deposition rate and film crystallinity in the specific reactor used in the present

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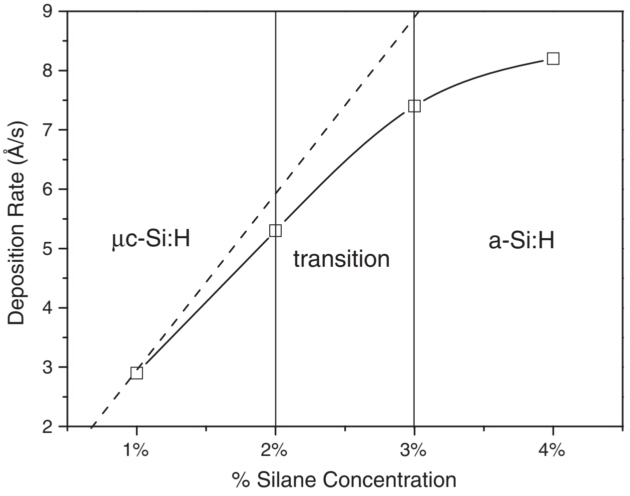

Fig. 1. Deposition rate (left axis) as a function of percent silane in the mixture.

investigation [5]. In this series of experiments, relatively high flow rates (400 sccm) were maintained while silane concentration was varied from 1% to 4%. Films of constant thickness (~1.6 μm) were deposited on Corning glass 7059 at a substrate temperature of 250 °C using electronic quality gases.

The total power dissipated in the discharge was maintained constant (72 mW/cm^2) as the fraction of SiH_4 in the gas mixture was increased. The amount of RF power actually fed into the discharge chamber was determined using an accurate method employing the Fourier transform determination of power and impedance phase, from current and voltage measurements [6]. Spatially Resolved Optical Emission Spectroscopy (SROES) measurements of electronically excited SiH* ($A^2\Delta$) and H_β were performed as described in Ref. [7], while the deposition rate was measured in situ using Laser Reflectance Interferometry [8]. Finally the film structure was examined using Laser Raman Spectroscopy.

3. Results and discussion

Different sets of electrical measurements were initially performed for the different silane molar fractions in order to find the exact electrical conditions leading to constant power dissipation in the discharge (72 mW/cm^2). The results show that there is a need for a slight increase of the applied voltage leading to an analogous drop of the discharge current as the silane content is increased from 1% to 4%. These variations can be attributed to a reduction of the electron mobility due to the increasing presence of the large SiH_4 molecules, having a substantially higher collision cross section than hydrogen.

Fig. 1 presents the variation of the deposition rate of the silicon thin films as a function of the %SiH_4 fraction in the gas mixture. The film growth rate increases with the %SiH_4 fraction up to 3% and then a much slower increase is observed. This enhancement is mainly the result of the increase of the production of SiH_x ($x=1,2,3$) radicals in the gas phase that is followed by an increase of the precursors' flux towards the substrate. The slower rate of increase above 3% is normally due to the consumption of the highly reactive radicals (SiH_2, SiH, Si) in secondary gas phase reactions with SiH_4. This is better illustrated using the dashed line in the figure, which results from a linear regression starting from zero and passing from the 1% SiH_4 in H_2 experimental value. The deviation of the other experimental values from this line is increasing with silane fraction, indicating the less rationalistic usage of the film growth precursors despite the higher deposition rates.

In addition, Fig. 1 includes the changes in the film structure with the increase of the %SiH_4. In the 1% case the films are highly crystalline (~85%), while the Raman spectra of the films deposited at 2% and 3% SiH_4 show important similarities. Namely, the Si–Si peak is located at lower wave numbers (501 cm^{-1}), indicating a significant reduction of the size of the crystallites [9,10], in agreement with most of the results concerning the transition from microcrystalline to amorphous silicon growth [11,12]. Finally, the Raman spectra show that the transition to amorphous silicon growth takes place for the gas mixture of ~3% SiH_4 in H_2.

It is remarkable that although the transition occurs at 3% SiH_4 we were not able to detect any indicative change in any of the electrical properties of the discharge (voltage, current and discharge impedance) in this region. This is a first indication that the transition is not strictly related to changes in the density or flux of charged species while it rules out the electrical measurements as a diagnostic tool for the prediction of the growth regime change. On the other hand, Optical Emission Spectroscopy (total or spatially resolved) has already been used by different groups and in various reactors [13–15] for predicting the transition from microcrystalline to amorphous silicon deposition. In our case, SROES was applied at the conditions presented above for recording the emission intensity of SiH ($A^2\Delta$–$X^2\Pi$) radicals together with the emission intensity of β-balmer line of H atoms. Both of these lines have shown to be sensitive in the variation of %SiH_4 in the gas mixture. Thus, Fig. 2 presents the time-averaged axial emission profiles of SiH* excited species. The increase of %SiH_4 leads to an enhancement of the SiH* production rate. In addition

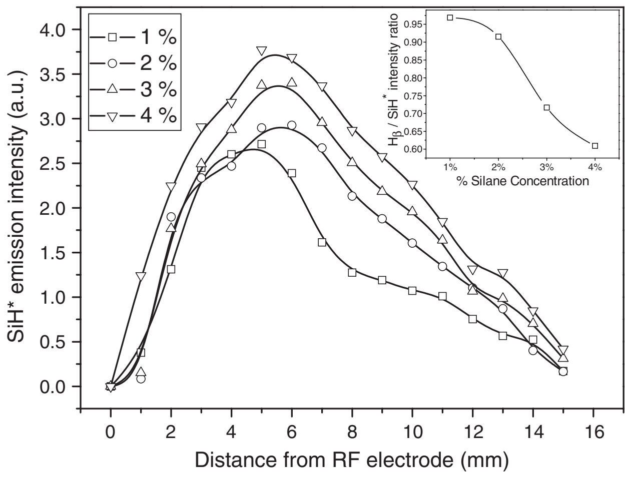

Fig. 2. Spatial distribution of SiH* radical at four different SiH_4 fractions in the gas mixture.

there is a displacement of the maximum rate of production towards the substrate as we go from 1% to 2% SiH_4 in the mixture. This is in agreement with a previous work of this group in another reactor that is used for the deposition of solar cells [13]. However, in this case of much lower total gas pressure and much higher electrode gap, the change of the emission profiles is not as clear as in Ref. [13].

Furthermore, the ratio of the total H_β to the total SiH* emission intensity that has been proposed by other groups as a method for predicting the transition from microcrystalline to amorphous silicon growth was also calculated by integrating the two emission profiles in space. The results are also included as an inset in Fig. 2 and show an abrupt drop of the ratio as we go from 2% to 3% SiH_4 in H_2 mixtures. This result in combination with the variation of the emission profiles indicates that SROES has the potential to be applied for the prediction of microcrystalline to amorphous silicon transition.

The results so far indicated that the transition from microcrystalline to amorphous silicon growth is mainly related to the variation of free radical fluxes rather than that of the charged species. In order to have a better estimation of the plasma parameters that are mainly responsible for the transition, we have performed calculations of the ion bombardment and the H atoms flux at the specific conditions as presented in the following paragraphs.

3.1. Ion flux and bombardment

The calculation of the ion flux and ion bombardment was performed by using an electrical model which is described in detail elsewhere [16,17]. Briefly, the model uses as an input the results of the electrical measurements and of the SROES and assumes that the mass transport of ions in the bulk is governed by ambipolar diffusion while in the sheaths is determined by their drift in the high field. The ion current and consequently the ion flux in the sheath of the powered electrode and the substrate holder are then calculated using the Child–Langmuir law for collisional sheaths, according to the relation:

$$J_i = \frac{2}{3}k\varepsilon_o\left[\frac{\overline{E}^{3/2}-\overline{E}_o^{3/2}}{x}\right] \tag{1}$$

where, $\overline{E}$ is the time averaged value of the sheath field at the position x, $\overline{E}_o$ is the value of the electric field at the plasma-sheath boundary ($x=0$), k the high field mobility-like factor and ε_o the dielectric constant. Assuming no ionization or charge recombination in the sheaths the average value of the distribution of the time-averaged field in the sheath can be written as:

$$\overline{E}(x)=\sqrt[3]{\left(\left(\overline{E}_d^{3/2}-\overline{E}_o^{3/2}\right)\left(\frac{x}{d}\right)+\overline{E}_o^{3/2}\right)^2} \tag{2}$$

where, d is the mean sheath thickness and E_d the field value at the electrode. Both E_d and d are calculated using the electrical measurements and more precisely from the total discharge current, while the value of E_o is calculated according to Ref. [18]. Thus, Fig. 3 (left axis) presents the variation of the ion flux (J_i/e) towards the substrate as a function of $\%SiH_4$ in the gas mixture, calculated using Eq. (1) and for $x=d$. It is observed that the ion flux decreases with silane fraction and this reduction is more pronounced from 3% to 4% as a result of the drop of both the high - field mobility-like factor and the electric field with increasing SiH_4 fraction.

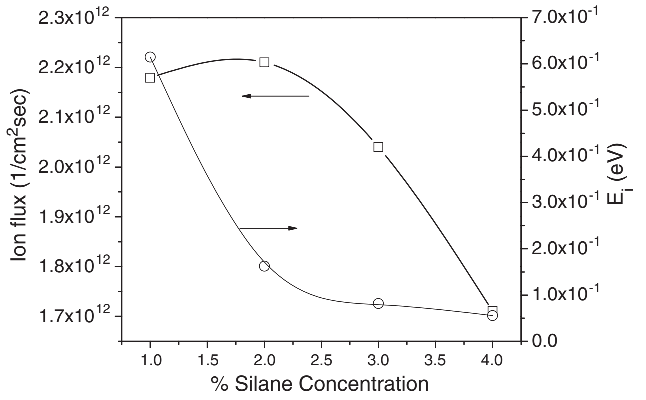

Fig. 3. Ion flux towards the growing surface (left axis) and energy transferred per monolayer per surface (right axis) as a function of silane fraction.

Having calculated the ion flux and the value of the electric field in the substrate, the total power density transferred from the ions to the growing thin film can be estimated by using the relation:

$$P_i=\frac{J_i}{2e}mu_i^2=\frac{J_i}{2e}mk^2E_d \tag{3}$$

where, m is the ion mass and u_i the drift velocity of ions at position $x=d$. Moreover, in order to include in our analysis the fact that the film growth rate is varied with SiH_4 fraction, the energy E_i transferred by the ions per thin film monolayer and per surface site, was calculated. This has been done by multiplying P_i by the time required for the formation of one silicon monolayer and the area defined by a Si–Si bond. The thickness of one monolayer was considered to be 10 Å while the Si–Si bond length was taken as 2.4 Å The results of these calculations are shown on the right axis of Fig. 3 and as one can observe there is an abrupt drop of E_i from 1% to 2% and after that the energy transfer remains almost unaffected. It is also remarkable that the predicted values of E_i are quite low (much lower compared to either the Si–Si or the Si–H bond strengths). This is mainly a result of the assumption that the interaction between ions and substrate includes only the transfer of kinetic energy. No charge transfer exchange was taken into account and this issue will be discussed later when the results concerning the H atoms flux will be presented and a comparison between the energy transferred by each species will be performed.

3.2. H atoms

In order to have an estimation of the effect of $\%SiH_4$ on the density and flux of H atoms towards the surface, the gas phase chemistry of these species was considered. The main

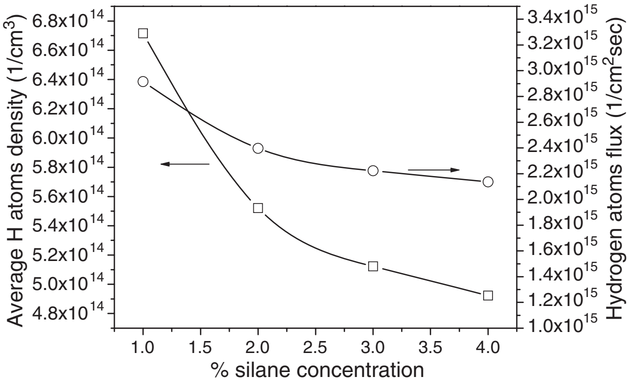

Fig. 4. Calculated average hydrogen atoms density (left axis) and hydrogen atoms flux towards the surface as a function of silane fraction.

mechanisms of H atoms production and consumption in SiH_4/H_2 discharges are summarized in the following reactions:

$$e^- + H_2 \rightarrow 2H + e^- \tag{R1}$$

$$e^- + SiH_4 \rightarrow SiH_x + (4-x)H + e^-(x = 0-3) \tag{R2}$$

$$H + SiH_4 \rightarrow SiH_3 + H_2 \tag{R3}$$

According to these reactions, the mass balance of H atoms in the discharge can be written as:

$$\frac{d\overline{N}_H}{dt} = 2k_1\overline{N}_e\overline{N}_{H_2} + 2k_2\overline{N}_e\overline{N}_{SiH_4} - k_3\overline{N}_H\overline{N}_{SiH_4} \tag{4}$$

where, $\overline{N}_H$, $\overline{N}_{H_2}$, $\overline{N}_{SiH_4}$ and $\overline{N}_e$ are the average density of hydrogen atoms, hydrogen molecules, silane and electrons and k_1, k_2, k_3 are the rate constants of R1, R2 and R3, respectively. For the calculation of the H atoms that are produced from silane electron impact dissociation, the branching ratio of the ion core model has been used that gives a value of ~2 H atoms for total SiH_4 dissociation. The differential Eq. (4) has the solution:

$$\overline{N}_H e^{\int_0^t k_3\overline{N}_{SiH_4dt}} = 2\int_0^t \left(k_1\overline{N}_e\overline{N}_{H_2} + k_2\overline{N}_e\overline{N}_{SiH_4}\right)e^{\int_0^t k_3\overline{N}_{SiH_4dt}}dt \tag{5}$$

which in turn for $\overline{N}_H=0$ at $t=0$ and for low silane conversion in the discharge gives an expression for the average hydrogen atoms of the form:

$$\overline{N}_H = 2\cdot\left(\frac{k_1\overline{N}_e}{k_3}\cdot\frac{\overline{N}_{H_2}}{\overline{N}_{SiH_4}} + \frac{k_2\overline{N}_e}{k_3}\right)\cdot \tag{6}$$

For the calculation of the silane and hydrogen electron induced dissociation rate constants a publicly available Boltzmann equation solver was applied [19]. The rate constants k_1 and k_2 were obtained by averaging the results of the solver over a wide range of electric field values from 80 to 200 V/cm. It is worth noting that the rate constant for silane dissociation predicted by the solver is about two orders of magnitude higher compared to the one of hydrogen and changes slightly with the fraction of SiH_4 in the mixture. The required average electron density was calculated by using the experimental measurements of the ohmic part of the discharge impedance according to Ref. [20], while the rate constant k_3 was taken from Ref. [21]. The average electron density was found to be almost constant in this range of SiH_4 fraction variation and a value of 8.5×10^8 cm^3 was used in all calculations. Using these values, an application of Eq. (6) gives the average density of H atoms in the discharge as plotted in Fig. 4 (left axis). The increase of SiH_4 percentage results in a drop of $\overline{N}_H$, which is determined by the decrease of the H_2/SiH_4 density ratio (term $\overline{N}_{H_2}/\overline{N}_{SiH_4}$ in Eq. (6)) or in other words it is due to the drop of the production of H atoms from (R1) relative to their consumption in (R3).

Furthermore, in order to calculate the flux of H atoms towards the substrate the spatial profile of H atoms density in the discharge was estimated as following a Gauss function of the form $G(x) = \beta e^{-2\left(\frac{x-d/2}{d^2}\right)^2}$, where β is the loss probability of H atoms in silicon surfaces [22] and d is the electrode gap. The flux towards the growing film was then calculated from the relation:

$$J_H = \overline{D}_H\overline{N}_H\left.\frac{dG(x)}{dx}\right|_{x=1.5}. \tag{7}$$

where, D_H is the diffusion coefficient of H atoms in the SiH_4/H_2 mixture.

The results of this calculation are presented on Fig. 4 (right axis) and as in the case of ions, hydrogen atoms flux is reduced with the $\%SiH_4$ in the gas mixture. However, the calculated H atoms flux is more than three orders of magnitude higher compared to the flux of ions (Fig. 3) over the entire range of $\%SiH_4$. This means that ion bombardment can play a role in the film structure and specifically in the transition from microcrystalline to amorphous silicon only if the energy that is transferred to the surface per ion is extremely higher compared to the energy per H atom. In order to study if this is possible it is better to consider the worst case for the H atoms and the most favorable one for the ions. In the case of ions the most efficient way of energy transfer is their recombination on the surface and an energy release equal to the ionization energy (~15 eV for hydrogen ions and ~11 eV for silicon ions). On the other hand, the worst scenario for H atoms is that their interactions with the surface do not include chemical reactions and only kinetic energy through collisions with the surface is exchanged. This is because all chemical reactions involving H atoms are exothermic with a rather high energy release. The kinetic energy of H atoms due to their thermal motion is about 0.01 eV and only with these two limiting cases the role of ions can be important in the transition from microcrystalline to amorphous silicon growth. Further work is in progress for the investigation of the effect of the substrate bias potential at conditions close to the transition that will clarify the importance of ions in the deposition process.

4. Conclusions

An investigation concerning the role of the main plasma parameters on the transition from microcrystalline to amorphous silicon growth and the possibility to apply plasma diagnostics for the prediction of this transition was performed.

The phase change was achieved by increasing the fraction of the silane gas mixture from 1% to 4% under constant power dissipation conditions.

The transition to amorphous silicon deposition takes place at 3% SiH_4 in H_2 and for a deposition rate of 7.5 Å/s. The electrical properties of the discharge were found to be unaffected during the growth regime change indicating that charged species do not play an important role in this transition and that electrical measurements cannot be used for predicting it. On the other hand, both spatial and total emission spectroscopy were found to be sensitive in the increase of silane fraction, especially for the gas mixtures of 2% and 3% of SiH_4 where the transition takes place. This observation indicates that emission spectroscopy has the potential to be applied for the prediction of the transition.

Furthermore, calculations of the effect of SiH_4 fraction on the ion and hydrogen atom fluxes to the growing film surface have shown that they both decrease with increasing %SiH_4 and this is followed by an analogous drop of the energy transferred to the surface. This decrease is much more important if one considers also that in these conditions the deposition rate is enhanced leading to a very important drop of the energy transferred per monolayer.

Finally, the flux of H atoms was found to be more than three orders of magnitude higher compared to that of ions, suggesting that the drop of the H atoms flux in combination with the increase of SiH_x flux and the deposition rate is responsible for the transition to the amorphous silicon growth. Ions would play a significant role in this process only if the energy transferred per ion is extremely higher compared to H atoms.

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References

[1] T. Roschek, T. Repmann, J. Müller, B. Rech, H. Wagner, J. Vac. Sci. Technol., A 20 (2002) 492.

[2] O. Vetterl, F. Finger, R. Carius, P. Hapke, L. Houben, O. Kluth, A. Lambertz, A. Muck, B. Rwch, H. Wagner, Sol. Energy Mater. Sol. Cells 62 (2000) 97.

[3] U. Kroll, J. Meier, A. Shah, S. Mikhailov, J.J. Weber, J. Appl. Phys. 80 (1996) 4971.

[4] S. Suzuki, M. Kondo, A. Matsuda, Sol. Energy Mater. Sol. Cells 62 (2000) 489.

[5] E. Katsia, E. Amanatides, D. Mataras, Á. Soto, G.A. Voyiatzis, Sol. Energy Mater. Sol. Cells 87 (2005) 157.

[6] N. Spiliopoulos, D. Mataras, D.E Rapakoulias, J. Vac. Sci .Technol., A 14 (1996) 2757.

[7] D. Mataras, S. Cavadias, D.E. Rapakoulias, J. Appl. Phys. 66 (1989) 119.

[8] E. Amanatides, S. Stamou, S. Boghosian, D. Mataras, in: Proceedings of the 16th European Photovoltaic Solar Energy Conference, Glasgow, UK, vol. 1, 2000, p. 581.

[9] H.S. Mavi, A.K. Sukla, S.C. Abbi, K.P. Jain, J. Appl. Phys. 66 (1989) 5322.

[10] Y. He, Y. Wei, G. Zheng, M. Yu, M. Liu, J. Appl. Phys. 82 (1997) 3408.

[11] C. Smit, R.A.C.M.M. van Swaaij, H. Donker, A.M.H.N. Petit, W.M.M. Kessels, M.C.M van de Sanden, J. Appl. Phys. 94 (2003) 3582.

[12] M. Jana, D. Das, Sol. Energy Mater. Sol. Cells 81 (2004) 169.

[13] E. Amanatides, D. Mataras, D. Rapakoulias, M.N. van den Donker, B. Rech, Sol. Energy Mater. Sol. Cells 87 (2005) 795.

[14] J.K. Rath, R.H.J. Franken, A. Gordijn, R.E.I. Schropp, W.J. Goedheer, J. Non-Cryst. Solids 338–340 (2004) 56.

[15] M. Kondo, M. Fukawa, L. Guo, A. Matsuda, J. Non-Cryst. Solids 266–269 (2000) 84.

[16] E. Amanatides, D. Mataras, J. Appl. Phys. 89 (2001) 1556.

[17] E. Amanatides, D. Mataras, D.E. Rapakoulias, J. Appl. Phys. 90 (2001) 5799.

[18] V.A. Godyak, N. Sternberg, Phys. Rev., A 42 (1990) 2299.

[19] BOLSIG (Shareware), Kinema Software (web site: http://www.siglo-kinema.com/bolsig.htm).

[20] E. Amanatides, A. Hammad, E. Katsia, D. Mataras, J. Appl. Phys. 97 (2005) 073303.

[21] J. Perrin, O. Leroy, M.C. Bordage, Contrib. Plasma Phys. 36 (1996) 3.

[22] A. Tserepi, T.A. Miller, J. Appl. Phys. 75 (1994) 7231.