

Electrical properties of composite silicon thin films

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Abstract - Amorphous-nano-crystalline silicon composite thin film (a-nc-Si:H) sample were synthesized by Plasma Enhanced Chemical Vapor Deposition technique. The electrical properties of thin film and measurement of DC conductivities were accomplished using Dielectric spectroscopy (Impedance Spectroscopy) in wide frequency and temperature range. In analysis of impedance data, two approaches were tested: the Debye type equivalent circuit with two parallel R and CPE (constant phase elements) and modified one, with three parallel R and CPE additionally interpreting crystal boundary effects. It was found that the later better fits to experimental results properly describing significant composite structure and crystal boundary dielectric effect with arbitrary hydrogen concentration indicating presence of strain. The amorphous matrix showed larger resistance and lower capacity than nano-crystal phase. Also it was found that composite silicon thin film cannot be properly describes by equivalent circuit only with resistors and constant phase elements in serial relation.

I. INTRODUCTION

It is natural that vast interest activation about silicon experimental and theoretical resources has been devoted to understanding its properties. Concerning third generation silicon thin film solar cells, its layers and device applications move inexorably to shorter length scales interface and surface characteristics gain in great importance. In analyze of silicon thin film properties it is desirable to explore the nature of chemical bonding not only the interface and surface of silicon layers but already include both static structural properties and kinetic aspects of its composites. A dark conductivity property of silicon thin film implies both aspects: static throe structural ordering issues and kinetic or dynamic properties revealed by impedance spectroscopy throe electrical properties.

The composite a-nc-Si:H thin films is mixed-phase material consisting of silicon nanocrystals embedded in amorphous silicon (a-Si:H) matrix. It has been the subject of intense research for variety of applications due to their unique optical and electrical properties [1]. Electrical and optical properties of a-nc-Si:H can be controlled by silicon nanocrystals size distribution and ratio of amorphous/nanocrystalline volume contribution. Measurements of the optical properties and structural analysis in previous published papers [2] showed that the spectral distribution of the absorption coefficient, in a wide range of crystal to amorphous fractions, can be maintained close to pure amorphous silicon in the visible

part of the spectrum and showed square dependence on the photon energy. The average optical gap was larger for smaller nano-crystals and a higher crystal fraction X_c just confirming the quantum size effects that correspond to quantum dots [3, 4].

Impedance spectroscopy (IS) has been widely used in last couple of years as a powerful technique for the study of the dielectric and conductivity behavior of ferroelectrics, ceramics, crystalline bulk and composite-crystalline silicon thin films [5, 6].

Because of silicon thin films composite form which is primarily characterized by the crystal fraction X_c and crystal grains sizes, it is necessary to understand effects of complex micro structural features on the overall electrical properties of thin films. The resistance and capacitance of crystals grains and grain boundaries, which is frequency and temperature dependent, can be evaluated from IS spectra. This technique for determination of the starting values for the basic equivalent electrical circuit were used in the fitting procedure of experimental impedance data with simulated data in order to select most appropriate equivalent circuit. This technique enables us to separate the real and imaginary component of the complex impedance and related parameters, and hence provides information of the structure-property relationship in the rated sample.

The sample examined by IS technique with composite structures with presence of crystals grains and grain boundaries embedded in matrix demonstrate complex impedance common in the event of two phase materials with different conductivity or permittivity. At high temperatures may occur two successive semicircle arcs mostly as a rule. These properties can conventionally be displayed in a complex plane plots (Nyquist diagram) in terms of the same formalism, refer to [5, 7].

The micro-structural properties revealed by techniques like grazing incidence X-ray diffraction (GIXRD) described in [4], Raman spectroscopy (RS) or X-ray powder diffraction (XRD) [2] are fundamental in composite silicon thin films investigations but the correlation between microstructure and electrical properties is not always obvious or straightforward. Electrical properties may vary in intrinsic material and are intensive to minor variations in structure and composition or whether the properties are extrinsic since they could vary dramatically if impurities are present, especially if impurities to the grain boundaries [8]. Thanks to impedance spectroscopy and appropriate data analysis it is

possible to characterize the different electrically active regions in a material, qualitatively by demonstrating their existence and quantitatively, by measuring their individual electrical properties. Identification and adoption of the most appropriate equivalent circuit for representation of the electrical properties is essential as a further step towards proper understanding sample properties. It has to be done in materials that are electrically particularly heterogeneous and where the impedance response of one part of sample overlaps, in frequency domain, with the response of other regions, giving rise to a composite response. Therefore, from an equivalent circuit model analysis the responses of the different regions may then be deconvoluted and characterized separately. The adequate model subsumes that are acquired simulation results have to be consistent with experimental data. This is, in most cases, based on designers experience on various equivalent circuit modeling.

II. MATERIALS CHARACTERIZATION

A. Experimental

Sample of amorphous-nano-crystalline thin film with a thickness of 100 nm were deposited by the PECVD method using radio frequency glow discharge in a capacitively coupled parallel plate reactor, as described earlier (Gracin, Thin Solid Films). Used gas mixtures consisted of 5% silane and 95 % hydrogen and the substrate was glass.

The electrical conductivity of the thin film was measured by impedance spectroscopy (Novocontrol Alpha-N dielectric analyzer) in the frequency range 0.01 Hz – 10 MHz and in the temperature range -100–120 °C. For the electrical contact, two gold electrode pads separated by 4 mm were sputtered on the sample surface using SC7620 Sputter Coater, Quorum Technologies. The impedance spectra were analyzed by equivalent circuit modelling using the complex non-linear least squares fitting procedure.

B. Measurement Data

Typical GIXRD data for measured sample titled G01 is described in previous paper [4]. The volume fraction of crystalline/amorphous phase, estimated from the ratio of integrated intensities under crystalline diffraction peaks and broad amorphous contributions, was about 30%. The average crystal size was estimated from the width of crystalline peaks using Scherrer formula assuming that the size broadening due to strain could be neglected comparing to the size broadening. In that way obtained values are the same as estimated from HRTEM micrographs just verifying the procedure.

III. EQUIVALENT CIRCUIT MODEL

There are various approaches to model non-ideality of electronically conducting materials such as amorphous

nano-crystalline materials. Since non-ideality of impedance response in silicon samples are observed, introduction of CPS is mainly instead of ideal capacity used in equivalent circuit modeling. Equivalent circuit model described in earlier paper [9] consisted of two $R_1||CPE_1$ and $R_2||CPE_2$ parallel elements in serial connection had provided correct picture and adoptable results. Calculated values adopted in fitting procedure represents well defined model with good alteration with experimental IS curves and defined equivalent circuit elements. But for better alteration of experimental results an improved equivalent circuit model must be presented to include proven strain in matrix according to arbitrary hydrogen concentration and therefore evidenced of crystal boundary effect – different dielectric region and prove of existing potential barrier. In that case an additional component will be added to basic structure and final impedance $\dot{Z}$ of modified complex equivalent circuit can be calculated according to literature [7] as:

$$\dot{Z} = \frac{A_1 R_1 (j\omega)^{n_1}}{R_1 + A_1 (j\omega)^{n_1}} + \frac{A_2 R_2 (j\omega)^{n_2}}{R_2 + A_2 (j\omega)^{n_2}} + \frac{A_3 R_3 (j\omega)^{n_3}}{R_3 + A_3 (j\omega)^{n_3}}, \quad (1)$$

Where $\dot{Z}(\omega) = \dot{Z}_1 + \dot{Z}_2 + \dot{Z}_3$ is impedance of tree $R||CPE$ parallel elements in serial connection representing mixed-phase material with notable crystal boundary effect between phases and therefore different structural and individual electrical properties. Figure 1 shows a sketch of a a-nc-Si:H film where region 1 corresponds to the amorphous, region 2 to the nano-crystal and region 3 to the crystal boundary interface components.

Other formalisms as complex admittance $\dot{Y}(\omega)$, complex permittivity $\dot{\epsilon}(\omega)$ complex modulus $\dot{M}(\omega)$ are describe and given in previous paper [7]. The relationship between them is given as

$$\dot{Z}(\omega) = 1/\dot{Y} = \dot{Y}^{-1}, \quad \dot{M}(\omega) = 1/\dot{\epsilon} = \dot{\epsilon}^{-1} \quad (2)$$

And

$$\dot{M}(\omega) = j\omega C_0 \cdot \dot{Z}, \quad (3)$$

Where omega is angular frequency ($\omega = 2\pi f$), $C_0 = \epsilon_0 A/d$ presents the capacitance of the measuring cell in vacuum without presence of sample where A is cell area and d is plate distance or sample thickness, respectively. Capacitance C_0 of a condenser with the geometry of the sample is calculated $C_0 = 6.95 \cdot 10^{-15}$ F.

Serial resistor R_s presenting measuring electrode resistance reasonable can be excluded in presented equivalent circuit model since its parameter is a few orders of magnitude less in comparison to sample DC resistance. Therefore its influence in numerical analysis can be negligible. Capacitance C_0 of a condenser with the geometry of the sample is also excluded in many discussions made in previous papers analyze [9-11]. However in presented modified equivalent circuit model calculated value C_0 is presented with equivalent capacity named C_1 and as a notable capacitive value it is taken in the consideration in fitting procedure. As a result of fitting steps C_1 will be evaluated as well.

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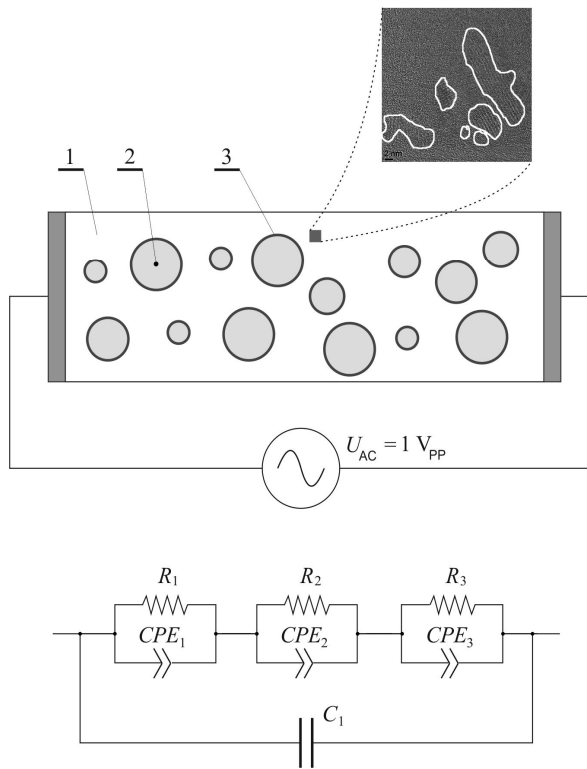


Figure 1. Sketch of the different components contributing to dark conductivity of composite sample connected to AC voltage and equivalent circuit model formed by impedances in series; 1–a-Si:H phase, 2–nc-Si:H phase, 3–Crystal boundary phase.

IV. EXPERIMENTAL RESULTS

Amorphous-nanocrystalline composite silicon thin film named G01 have been investigated in the frequency range 0.01 Hz – 10 MHz using 80 steps and 1V_{pp} of modulation in the temperature range from -100 °C to 120 °C. Experimental impedance data of named sample shows semicircle arcs in three temperature cases: 80 °C, 100 °C and 120 °C [9]. Interpreting the results of AC IS experiment to give information on electrical properties (DC conductivity) or microstructure picture as existence of phases, especially for complex materials like a-nc-Si:H requires a kind of complex approach.

Predominate opinion interprets experimental IS results of composite silicon thin film in terms of series or parallel combinations of resistors and capacitors and special elements like the CPE. It is not proven yet that the complex topology of real nano-structures can be described by using other elements in combination with R-CPS series and parallel ideas. Physically is not possible to consider the complex microstructure as either a parallel or a series arrangement of phases. Rather, since the current must flow according to some arbitrary frequency through amorphous lower-conducting phase in some percolation effective path and through higher-conducting nanocrystalline phase, there is a degree of tortuosity

present, which gives a more complicated, IS response. This anisotropic structure influences electronic transport, since carriers flowing between crystals (conduction path in Figure 2) will encounter more crystals boundaries then when flowing through high resistance a-Si:H matrix.

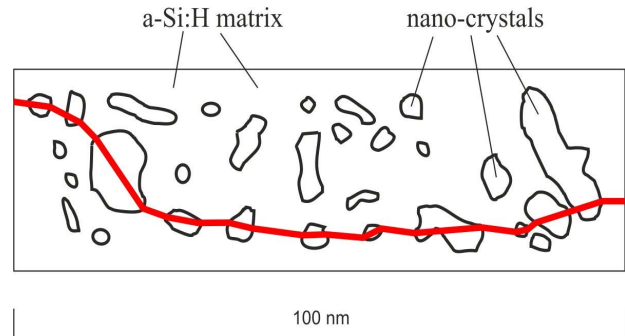


Figure 2. Geometrical model of sample G01 structure derived from HRTEM [9]. Red line represents arbitrary conduction path - effective current path on some arbitrary frequency through composite structure.

The total resistance of the circuit can easily be read from the $Z''(Z')$ curve. The presented spectrum allows clearly determination only dominant resistance amorphous phase R_1 at the beginning of the fitting procedure. Different relaxation time or time constants are detected based on peaks plots of $Z'' = \log(f)$ and electric modulus $M'' = \log(f)$, $(1/\omega_{\max})_1 = \tau_1 = A_1 R_1$ and further on [7]. $-Z''$ and M''/C_0 plotted versus frequency f show two peaks for thin film sample G01. Since $-Z''_{\max}$ correspond to R_2 and M''/C_0 correspond to $1/2C_1$, the conductivity and the capacitance values were determined [6, 7].

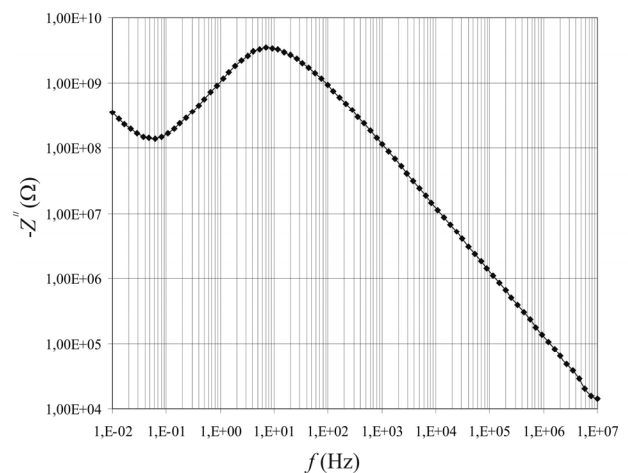


Figure 3. $-Z''$ plot versus frequency (f) of a-nc-Si:H sample G01 at temperature 120 °C.

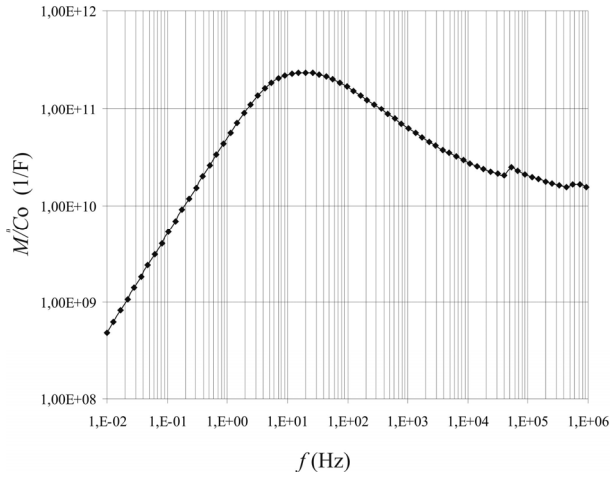


Figure 4. M''/C_0 plot versus frequency (f) of a-nc-Si:H sample G01 at temperature 120 °C .

Depending on the frequency one of the components dominates in serial connection giving us possibility to obtain its resistance R and CPE value - capacitance A .

It is possible that inclusion geometry capacitance of metal-contact interface and porous oxide influence contact/film layer also contributes to determining complexity of arcs in the impedance spectrum, and not just materials series or parallel character. But this influence is not discussed of this study.

In the IS data the dominant amorphous phase is presented by parallel R_1 and CPE_1 element and evaluated with data from Table I, especially amorphous resistance $R_1=7.27$ G Ω and amorphous capacitance $A_1=1.5$ pF as it was shown earlier in [9]. Calculated capacitance of $A_1=1.25$ pF from theoretical relation M''/C_0 which corresponds to value $1/2C_1$ is in good agreement with calculated one. Exponent index n_1 as no-ideality index of impedance semicircle arcs at investigated temperature 120 °C is calculated as 0.937. This index points up the inhomogeneous amorphous structure reach of dangling bonds and hydrogen atoms earlier revealed by techniques like grazing incidence X-ray diffraction (GIXRD).

Nanocrystalline-phase resistance $R_2=0.877$ G Ω is order of magnitude lower than amorphous resistance as expected. Additional nc-Si:H phase capacitance A_2 evaluated as 3.4 pF (shown in Table II) can be expressed only according to M''/C_0 , $M'' = f(M')$ and $M'' = \log_{10}(f)$ plots. This capacitance suggests existence of second present phase: reach nanocrystalline phase. Its existence is previously evaluated thru volume fraction index $X_c=33$ % [11, 12]. Consequently this is not just one particular crystal size or distribution influence to overall capacitance. Nanocrystalline phase calculated capacitance $A_2 = 3.4$ pF of a-nc-Si:H sample suggests complex connection of nano-sizes individual crystals whit substantially higher capacity than amorphous phase ($A_1=1.5$ pF). Furthermore, no-ideality index n_2 is calculated as 0.89. This value reveals reach capacitive

TABLE I. CALCULATED VALUES EXTRACTED FROM EXPERIMENTAL IMPEDANCE DATA

Impedance plot data	Data index / units	Values
Total equivalent resistance	$R_p / G\Omega$	8.11
Specific sample resistance	$\rho_p / \Omega m$	811
Specific sample conductivity	$\sigma_p / \mu S cm^{-1}$	12.33
Amorphous-phase resistance	$R_1 / G\Omega$	7.27
Amorphous-phase specific resistance	$\rho_1 / \Omega cm$	72700
Amorphous-phase specific DC conductivity	$\sigma_1 / \mu S cm^{-1}$	13.85
Amorphous-phase dark pre-factor	$\sigma_{01} / k S cm^{-1}$	12.2
log (freq.) plot maximum	$\log_{10} f_{2max} (Z)$	0.875
Frequency maximum	f_{1max} / Hz	7.499
Amorphous-phase Relaxation time	$1/\omega_{1max} / sec.$	0.0212233
Amorphous-phase non-ideality index	n_1	0.937
Amorphous-phase capacitance	A_1 / pF	1.5
Fitted Measuring cell capacitance	C_1 / pF	0.005

TABLE II. CALCULATED VALUES EXTRACTED FROM EXPERIMENTAL MODULUS DATA

Modulus plot data	Data index / units	Values
Nanocrystalline-phase resistance	$R_2 / G\Omega$	0.877
Nanocrystalline-phase specific resistance	$\rho_2 / \Omega cm$	87.7
Nanocrystalline-phase specific DC conductivity	$\sigma_2 / \mu S cm^{-1}$	114.2
Nanocrystalline-phase dark pre-factor	$\sigma_{02} / k S cm^{-1}$	304
log (freq.) plot maximum	$\log_{20} f_{1max} (Z)$	1.25
Frequency maximum	F_{2max} / Hz	17.78
Nanocrystalline-phase Relaxation time	$1/\omega_{2max} / sec.$	0.00895
Nanocrystalline-phase non-ideality index	n_2	0.89
Nanocrystalline-phase capacitance	A_2 / pF	3.4
Boundary-phase resistance	$R_3 / G\Omega$	0.013
Boundary-phase capacitance	A_3 / pF	2
Boundary-phase non-ideality index	n_3	0.83

nature of its phase since its value is significantly lower than one.

Based on introduced improved equivalent circuit model which consists of three $R||CPE$ elements, existence of additional capacitance $A_3=2$ pF suggests presence of third dielectrically phase in investigated composite material. More likely it is a boundary effect of existing potential barriers arising from the resulting space charge layer at the silicon crystals boundaries crowded with hydrogen atoms. Also another parameter which proves the specific material dielectrically properties is non-ideality index of this phase – n_3 . In fitting procedure it is estimated as 0.83. This index clearly indicates different dielectric properties of its phase - more likely a quarter of nanometer wide boundary regions around formed silicon crystals formed by hydrogen atoms and therefore a weak dangling bonds presence. Another evidence of different dielectric region inherent as silicon crystals boundaries can be annotate three boundary phase resistance R_3 . Evaluated value $R_3=13$ M Ω is significantly lower than amorphous resistance $R_2=877$ M Ω proving thin hydrogen dielectric layer. Also, effective capacitance of measuring electrodes is fitted as $C_1 = 5 \cdot 10^{-15}$ F despite of its nominal value $C_0 = 6.95 \cdot 10^{-15}$ F as result of the sample geometry calculation published in [9]. It means that equivalent capacity of measuring electrodes is little bit smaller than expected. It is also prove of effective current path between electrodes despite of its geometrical shape.

It is common opinion that hydrogen presence in this region can be overcome by thermal treatment - annealing. These phenomena can be noted according to hydrogen atom redistribution in porous matrix and weak dangling bonds crystal boundary regions and predictable structural change phenomena in composite silicon thin films described elsewhere [13, 14].

All calculations based on experimental data and fitting curves on impedance and modulus data according to equations (1), (2) and (3) are shown in TABLE I and TABLE II.

V. CONCLUSION

The electric properties of amorphous-nanocrystalline silicon composite thin film were studied in a wide frequency range at different temperatures. The impedance response of a-nc-Si:H sample G01 were interpreted in terms of model of equivalent circuit with tree parallel R and CPE elements connected in serial. By the analysis of equivalent circuit impedance, combined with the analysis of experimental data of electrical modulus, it was possible to extract the resistance and capacitance contribution of all regions to the overall electrical properties of silicon composite thin films. Better model of equivalent circuit is established in the fitting process of experimental impedance data. Multi-arc behavior of experimental results had proved presumption of multi-phase existence, series arrangement of dominant amorphous and nanocrystalline phase with clearly evidence of crystal boundary effects. The non-ideality parameter $n_2 = 0.89$ highlights the capacitive nature of composite structure reach of nano-crystals embedded in amorphous matrix while another index $n_3 = 0.83$ highlights different dielectric properties of boundary

regions around formed silicon crystals. The amorphous phase resistance is higher than the same of nano-crystals while a-Si:H capacitance is smaller than capacitance in nc-Si:H phase. Impedance peak against frequency is proportional to the resistance of the composite material, while the peak of electrical modulus against frequency is inversely proportional to the existing capacitance, determining equivalent circuit parameters.

So far, the observed additional specificity in the electrical and structural properties can be explained as a consequence of hydrogen effusion and redistribution in the porous film forming boundary regions around crystals with arbitrary concentrations. The analysis of the IS data confirmed that crystals and its boundary effect has great contribution in the silicon thin film sample resistance and therefore consequently its conductivity.

However, the goal of this work is quite ambitious in its choice of equivalent circuit model to be represented, and the simplicity of model investigated here may prove to be a limitation on its ultimate quantitative success. In any case, a detailed comparison of dynamical results extracted from a well-defined model, such as one derived here, and carefully measured experimental properties on acceptable temperatures will inevitably lead to a deeper understanding of silicon-hydrogen surface chemistry, interactions and coexistence in silicon thin films.

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