

## CHARGE TRANSPORT IN MICROCRYSTALLINE SILICON, RELATION TO THIN FILM SOLAR CELLS

J. Kočka<sup>1\*</sup>, A. Fejfar<sup>1</sup>, H. Stuchlíková<sup>1</sup>, B. Rezek<sup>1</sup>, A. Poruba<sup>1</sup>, M. Vaněček<sup>1</sup>,  
P. Torres<sup>2</sup>, J. Meier<sup>2</sup>, N. Wyrsh<sup>2</sup>, A. Shah<sup>2</sup>, A. Matsuda<sup>3</sup>

<sup>1</sup> Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Prague 6, Czech Republic  
phone +420-2-24311137, fax +420-2-3123184, \* e-mail: kocka@fzu.cz

<sup>2</sup> Institut de Microtechnique, Université de Neuchatel, rue Breguet 2, CH-2000, Neuchatel, Switzerland  
phone +41-32-7183200, fax +41-32-7183201

<sup>3</sup> Electrotechnical Laboratory, Umezono, Tsukuba, Ibaraki 305, Japan, phone +81-298-58-5252, fax: +81-298-58-5425

**ABSTRACT:** Frequency spectra of A.C. conductivity allowed us minimization of the influence of the contacts and better understanding of the charge transport in microcrystalline silicon ( $\mu\text{-Si:H}$ ) solar cells. We were able to distinguish growth conditions for which the  $\mu\text{-Si:H}$  transport becomes anisotropic. We show how the size of crystallites influences charge transport path and thus probably the open circuit voltage of the cells. The A.C. measurements may become important tool for optimization of the  $\mu\text{-Si:H}$  solar cells.

**Keywords:** Microcrystalline Si -1; Photoelectric properties -2; a-Si -3

## 1. INTRODUCTION

At present hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) has become one of the most perspective materials for tandem thin film solar cells with a single-junction cell efficiency reaching over 7% [1]. High performance of the  $\mu\text{-Si:H}$  solar cells is due to enhanced optical absorption (about 3 times higher than crystalline silicon), to its stability with regard to light-induced degradation and to efficient photogenerated carriers collection. However, complicated microstructure, inhomogeneity (grains plus surrounding amorphous tissue) and so possible anisotropy of the  $\mu\text{-Si:H}$  are the reasons why little is known about the carrier collection mechanism.

Some of the available transport data (e.g. dark and photo-conductivity, Hall mobilities) were measured with coplanar electrodes (see [2]). In this case the influence of contacts is usually negligible and material transport properties along the substrate can be evaluated.

Measurement of transport perpendicular to the substrate (important for solar cells) has to be done in sandwich geometry and the results are inevitably influenced by contacts. However, even in this case we can find the "true" band-like conductivity from the characteristic plateau in the frequency dependence of complex A.C. conductivity measured in a wide frequency range (10 Hz - 10 MHz) if in parallel so called effective permittivity [3] approaches Si relative permittivity value  $\approx 11$ . We have used this approach to follow the degradation in hydrogenated amorphous silicon (a-Si:H) and proved that the changes of conductivity due to degradation of the intrinsic layer in the middle of a-Si:H based p-i-n solar cell is the same as deduced from coplanar measurement of intrinsic a-Si:H layer [4].

In an isotropic material (like a-Si:H [5]) the conductivities deduced in both sandwich and coplanar geometries should be and are the same [4].

In this paper we illustrate that the "true" dark conductivity measured in the sandwich and coplanar geometry for a series of  $\mu\text{-Si:H}$  samples can systematically differ, giving so the first experimental proof of the transport anisotropy in  $\mu\text{-Si:H}$ . For growth conditions leading to

isotropic  $\mu\text{-Si:H}$  both conductivities are close. The correlation of the conductivity with the grain morphology deduced from light scattering effects in the constant photocurrent method (CPM) [6] or directly by atomic force microscopy (AFM) is observed and its relation to the efficiency of the cells is discussed. Finally, we suggest a model of the transport path explaining the experimental data.

## 2. EXPERIMENT

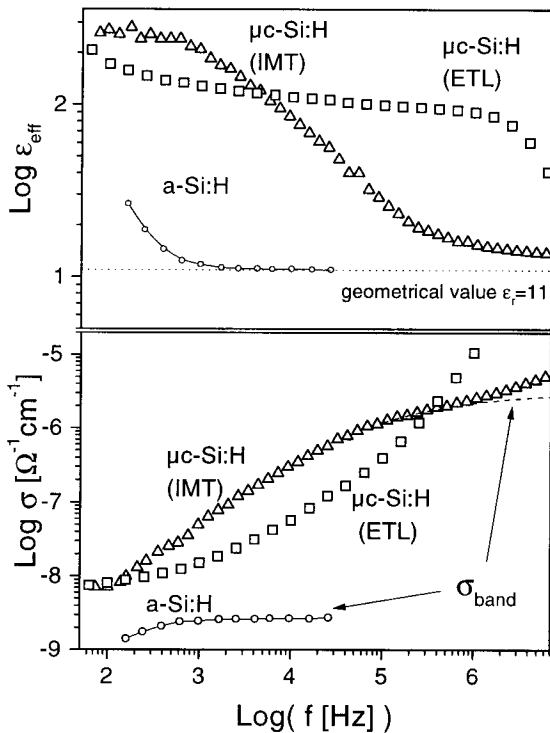
We have used  $\mu\text{-Si:H}$  samples from Institute de Microtechnique (IMT), Neuchatel prepared in two series with changing glow discharge power at 5% or 7.5 % dilution of silane in hydrogen. Silane was delivered through the gas purifier and the dilution ratio was determined as the silane part of the total gas flow  $\text{SiH}_4+\text{H}_2$ . Power at the excitation frequency 130 MHz delivered to the discharge ranged from 9 to 30 W for the 5% series and from 20 to 70 W for the 7.5% series (higher powers were needed to achieve the growth of microcrystalline silicon at this dilution). The layers with thicknesses around 2.5  $\mu\text{m}$  were deposited on Asahi glass covered by TCO (type U) kept at about 220° C. The details of preparation are described in ref. [7].

In order to compare  $\mu\text{-Si:H}$  layers from different laboratories we have also measured sample from Electrotechnical Laboratory (ETL), Tsukuba (deposited on ZnO coated glass by pulsed 40 MHz discharge modulated by 10 kHz and average power 65W, silane dilution ratio 2% and thickness 3  $\mu\text{m}$ ) which is compared with previously extensively characterized [2] 5.6  $\mu\text{m}$  thick IMT Neuchatel sample in Fig.1.

For sandwich electrical measurements we have deposited top semitransparent NiCr contacts with 1 mm diameter.

For A.C. conductivity measurements at room temperature in air or in a cryostat (25 - 450K) we have used the HP 4192A impedance analyzer (5 Hz - 13 MHz). For evaluation of D.C. conductivity Keithley 237 has been used.

We have used Omicron AFM to obtain the morphology of the  $\mu\text{-Si:H}$  surfaces and constant photocurrent method (CPM) to evaluate the contribution of the light scattering in the volume or on the surface of the films [6].



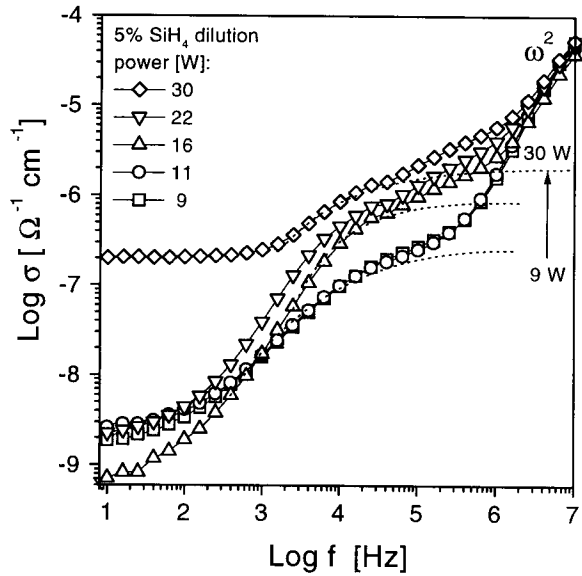
**Figure 1** Effective permittivity  $\epsilon_{eff} = C_m \cdot d / S \cdot \epsilon_0$  calculated from measured capacitance  $C_m$  (see text) and A.C. conductivity as a function of frequency of  $\mu c$ -Si:H layers prepared in IMT Neuchatel ( $d=5.6 \mu m$ ) and in ETL Tsukuba ( $d=3 \mu m$ ) in comparison with a-Si:H [4].

**3. RESULTS**

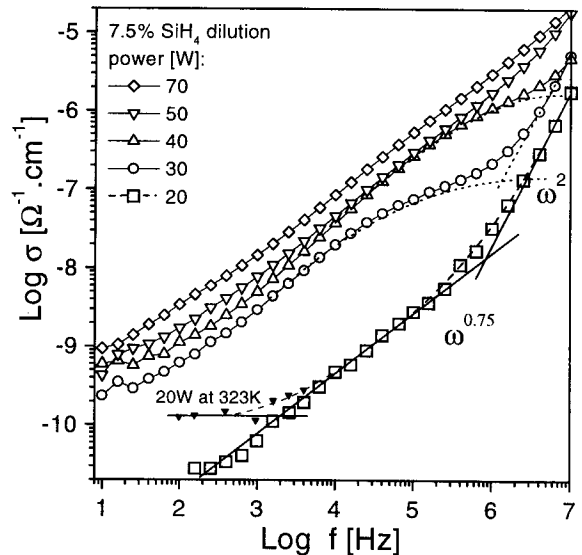
The results of the A.C. conductivity observed on different  $\mu c$ -Si:H samples are in the Figs.1-3, together with data for a-Si:H sample (taken from the above mentioned ref [4]).

In the simplest approximation we can simulate the complex A.C. conductivity of the sandwich sample with metal (ITO) contacts as a series combination of contact (depleted) region resistance and capacitance ( $R_C, C_C$ ) and bulk region resistance and capacitance ( $R_B, C_B$ ) which results in measured quantities ( $R_m, C_m$ ). At low frequencies the measured quantities are controlled by contact region(s). Therefore the observed capacitance is higher than geometrical value and the conductivity is limited by the depleted region(s). As the frequency increases the "true" bulk properties prevail. The observed capacitance  $C_m$  becomes close to the geometrical value. If at the same frequency range frequency independent "band-like" conductivity prevails there is a "plateau" in conductivity - this is the "true" conductivity of the material perpendicular to the substrate. At still higher frequencies the series sheet resistance ( $R_S$ ) of the contacts starts to play a role and leads to apparent increase of the conductivity  $\approx \omega^2$ .

To be able to compare the capacitance values for different samples in the top part of Fig. 1, we plotted them in the form of the effective permittivity  $\epsilon_{eff} = C_m \cdot d / (S \cdot \epsilon_0)$  where  $d$  is the sample thickness,  $S$  its area and  $\epsilon_0$  the vacuum permittivity. For a-Si:H the plateau in conductivity appears (see bottom part of Fig. 1) and  $\epsilon_{eff}$  approaches 11 in the kHz range. While for IMT  $\mu c$ -Si:H sample the conductivity



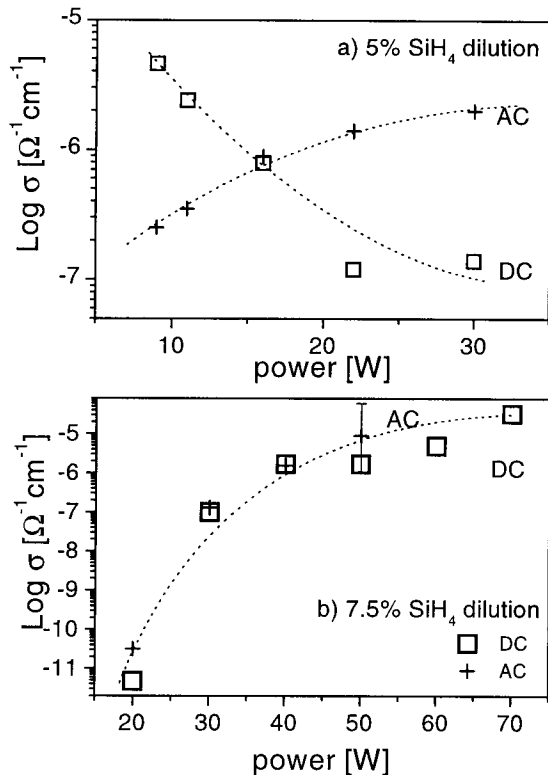
**Figure 2** Room temperature A.C. conductivity for 5% dilution series of  $\mu c$ -Si:H samples as a function of frequency. "Plateau" values of  $\sigma$  (see text) are indicated by dotted lines.



**Figure 3** Room temperature A.C. conductivity for 7.5% dilution series of  $\mu c$ -Si:H samples as a function of frequency. "Plateau" values of  $\sigma$  are indicated by dotted lines. Note that 20 W sample was amorphous (see text).

plateau and  $\epsilon_{eff} \approx 11$  appears in MHz range, for ETL sample, probably due to different microstructure and overall higher conductivity, the plateau and  $\epsilon_{eff} \approx 11$  is at room temperature out of range of our bridge.

The wide variation of results is typical for  $\mu c$ -Si:H which can have very different microstructure depending on the deposition conditions. In order to understand the differences we concentrated to the two IMT series of  $\mu c$ -Si:H samples prepared with different discharge power. The results are shown in Fig. 2 (for series with 5%  $SiH_4$  dilution) and Fig. 3 (for series with 7.5%  $SiH_4$  dilution). The systematic study of more ETL samples is in progress, too. In the case of 7.5% dilution higher powers are needed to obtain the microcrystalline layers (the sample prepared at 20W is amorphous). Note different conductivity of this a-Si:H



**Figure 4** Comparison of the perpendicular A.C. "plateau" conductivity (+) and D.C. coplanar conductivity (□) for 5% (a) and 7.5% dilution series (b) of  $\mu\text{c-Si:H}$  samples as a function of discharge power (see text).

sample (Fig. 3) which for today's "device grade" material is about 2 orders of magnitude lower than typical values of a-Si:H prepared 10 years ago (Fig. 1). Due to the small band conductivity of this a-Si:H sample, another conductivity mechanism (temperature independent hopping proportional to  $\omega^{0.75}$  at the medium frequency range  $10^3 - 10^5$  Hz) can be observed. In order to observe the "plateau" corresponding to the frequency independent band-like conductivity we had to heat the 20W (a-Si:H) sample above the room temperature (see curve at 323 K).

The plateau corresponding to the thermally activated band-like conductivity shifts with increasing temperature to higher  $\sigma$  values and frequency range. From A.C. conductivity at different temperatures (not shown here) we were able to deduce the activation energy of the band-like conductivity in the  $\mu\text{c-Si:H}$  samples and the conductivity prefactor.

#### 4. DISCUSSION

The comparison of the band-like A.C. conductivity (perpendicular to the substrate " $\perp$ ") with D.C. conductivity (along the substrate " $\parallel$ ") is shown in Fig. 4 for both 5% and 7.5% dilution series.

For 5%  $\mu\text{c-Si:H}$  series (Fig. 4a) not only the conductivity perpendicular to substrate ( $\sigma_{AC}$ ) and parallel to substrate ( $\sigma_{DC}$ ) are different but, moreover, with changing power the opposite trend is observed, which means that with increasing power the transport normal to the substrate is getting easier. This indicates that  $\mu\text{c-Si:H}$  structure is highly oriented (columnar?) and transport anisotropic, with anisotropy

changing with preparation conditions. This nicely agrees with the results of X-ray diffraction study which showed that the 5% series had a pronounced 220 texture [8]. To our knowledge this finding is the first experimental proof of the transport anisotropy in  $\mu\text{c-Si:H}$ .

Contrary to it for the 7.5% dilution series the values of  $\sigma_{AC}$  and  $\sigma_{DC}$  are very close (Fig. 4b). This indicates that these  $\mu\text{c-Si:H}$  samples are isotropic, without clear orientation. This again nicely agrees with the X-ray diffraction study [8].

How are the transport properties related to solar cell function? While efficiency of 7.5% dilution series based cells is highest for 30-40 W samples and decreases with increasing power from 40 to 70W (as well as photocurrent and electron drift mobility [9]) the conductivity increases (see Fig. 4).

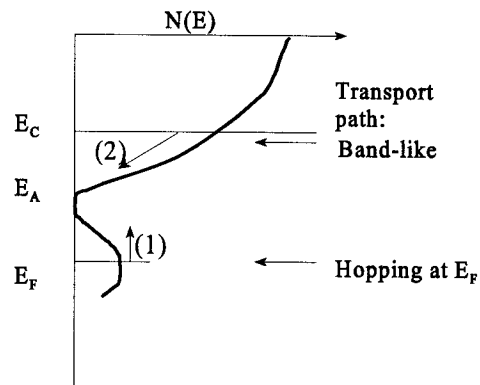
This is related to substantially decreasing conductivity activation energy  $E_a$ , see Table I. This could mean that the Fermi energy is shifting closer to the conduction band edge (see Fig. 5 - arrow (1)). However, the value of the conductivity prefactor  $\sigma_0$  is also substantially decreasing (see Table I.) and therefore we speculate that at least partly the decrease of the activation energy is due to the shift of the transport path deeper into localized states (see Fig. 5, arrow (2)).

**Table I.** Comparison of A.C. ( $\perp$ ) and D.C. ( $\parallel$ ) conductivity parameters (activation energies  $E_a$  and prefactor  $\sigma_0$ ) for selected  $\mu\text{c-Si:H}$  samples.

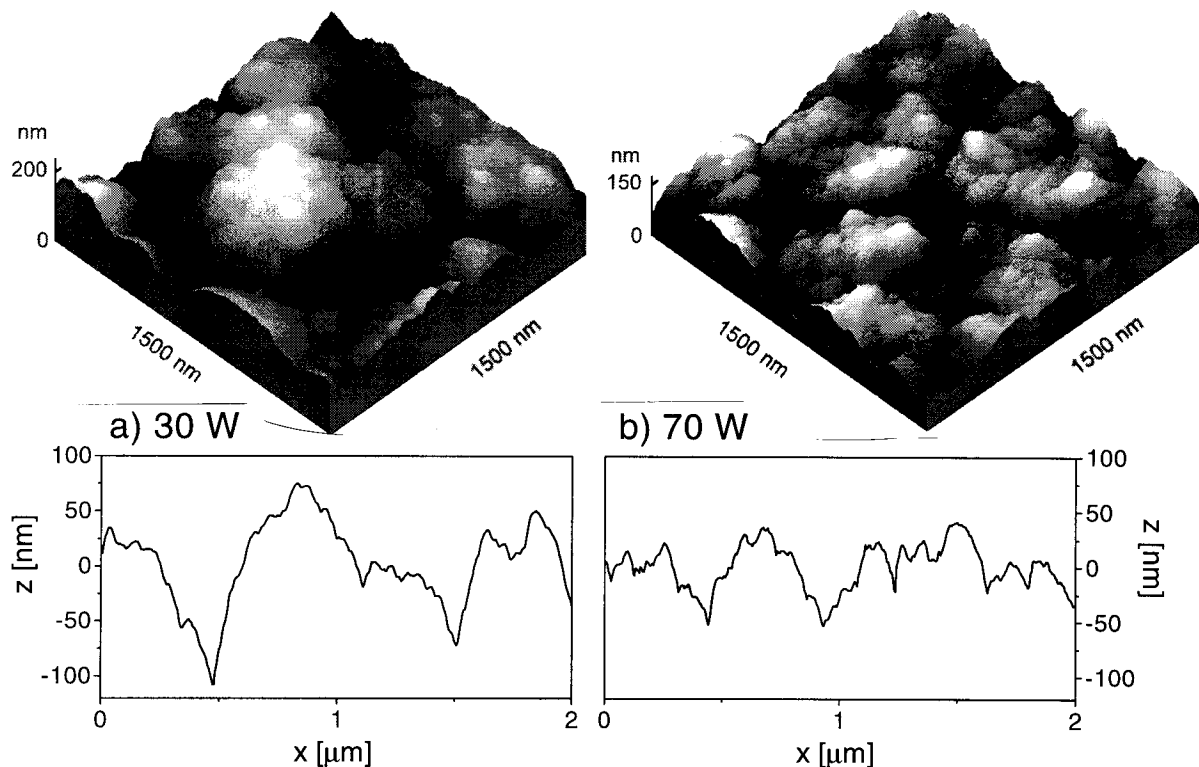
Power [W]	20 (a-Si:H)	30	70
$E_a^{AC}$ [eV]		0.57	0.17
$E_a^{DC}$ [eV]		0.42	0.15
$\sigma_0^{DC}$ [ $\Omega^{-1}\text{cm}^{-1}$ ]	108	9.3	0.1

The reason for downward shift of transport path could be increasing number of smaller and smaller grains, which leads to the increase of "tail-like" grain boundary states. This agrees well with decreasing mobility [9]. The downward shift of transport path naturally explains the decreasing  $V_{OC}$  of corresponding cells [7].

This finding is further supported by the morphology of



**Figure 5** Schematic picture of the density of states  $N(E)$ .  $E_C$  - conduction band edge,  $E_A$  bottom of tail,  $E_F$  Fermi level. Arrow (1) indicates possible upward shift of  $E_F$ , arrow (2) a downward shift of the transport path.



**Figure 6** AFM morphology of 30 W (left) and 70 W (right)  $\mu\text{c-Si:H}$  samples of 7.5% dilution series and corresponding height profiles.

the surface of the  $\mu\text{c-Si:H}$  as observed by AFM. In Fig. 6 the morphologies of the samples prepared at 30W (left) and 70W (right) are shown together with the corresponding height profiles. We can see that the 30 W sample has surface with larger and smoother crystalline grains. The root-mean-square roughness found from the AFM observed topography was 39 nm for the 30W sample and 22 nm for the 70 W sample, agreeing well with the values found from the light scattering effects in CPM [6].

## 5. CONCLUSIONS

We have demonstrated on a series of different  $\mu\text{c-Si:H}$  samples prepared in different laboratories that the A.C. conductivity is a useful tool for study of transport properties of  $\mu\text{c-Si:H}$  perpendicular to the substrate, important for function of solar cells.

We have proved that under certain conditions of  $\mu\text{c-Si:H}$  preparation (for example 5% silane dilution) the transport is anisotropic, due to highly oriented (columnar?) growth.

For 7.5% dilution the  $\mu\text{c-Si:H}$  transport properties are isotropic, by changing discharge power only the grain size is changing, as clearly illustrated by AFM pictures.

The change of grain size has strong influence on the energy position of dominant transport path, which on the other hand is closely related with the basic parameters of solar cells, namely  $V_{oc}$ .

## REFERENCES:

- [1] J. Meier, P. Torres, R. Platz, S. Dubail, U. Kroll, J.A. Anna Selvan, N. Pellaton Vaucher, Ch. Hof, D. Fischer, H. Keppner, A. Shah, K.-D. Ufert, P. Giannoulès, J. Koehler, MRS Spring Meeting, San Francisco 1996, MRS Proc. 420 (1996) p.3
- [2] A. Fejfar, N. Beck, H. Stuchlíková, N. Wyrsh, P. Torres, J. Meier, A. Shah, J. Kočka, Proc. of the 17<sup>th</sup> ICAMS Budapest, 1997, to be published in J. Non-Cryst. Solids.
- [3] J. Kočka, A. Fejfar, H. Stuchlíková, Technical Digest of 11<sup>th</sup> Sunshine workshop, 26 January 1998, Shinjuku, Tokyo, Japan.
- [4] J. Kočka, M. Vaněček, O. Štika, Q. Dung Tring, J. Stuchlík, A. Tříška, Proc. of the 8<sup>th</sup> EC PVSEC Florence 1988, Kluwer Acad. Publ., Dordrecht (1988), p. 724.
- [5] J. Kočka, E. Šípek, O. Štika, H. Curtins, G. Juška, J. Non-Crystalline Solids 114 (1989) 336.
- [6] A. Poruba, Z. Remeš, J. Špringer, M. Vaněček, A. Fejfar, J. Kočka, J. Meier, P. Torres, A. Shah, this conference
- [7] P. Torres, H. Keppner, J. Meier, U. Kroll, N. Beck, and A. Shah, phys. stat. sol. (a) 163, R9 (1997); and M. Goerlitzer, P. Torres, N. Beck, N. Wyrsh, U. Kroll, H. Keppner, J. Pohl and A. Shah, to be published in J. Non-Cryst. Solids (ICAMS 17) 1997.
- [8] P. Torres, J. Meier, U. Kroll, N. Beck, H. Keppner, A. Shah, Proc. 26<sup>th</sup> IEEE PVSC (1997), Anaheim (CA), p. 711-714.
- [9] J. Kočka et al., to be published.

## ACKNOWLEDGEMENTS:

This work was supported by EC-NEST project, by NEDO contract and by GAAV CR A1010809.