Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 3 (2011) 51–57
Energy Procedia
www.elsevier.com/locate/procedia

Symposium C: Materials, devices and economics issues for tomorrow's photovoltaics

Capacitance study of thin film SnO_2:F/p-type a-Si:H heterojunctions

G. Cannella[a,*], F. Principato[a], M. Foti[b], C. Garozzo[c], S. Lombardo[c]

[a]*Dipartimento di Fisica e Tecnologie Relative, University of Palermo, Building 18, Viale delle Scienze, 90128 Palermo, Italy*
[b]*STMicroelectronics, Stradale Primosole, 50, 95121 Catania,Italy*
[c]*CNR-IMM, Zona Industriale, Ottava Strada, 5, 95121 Catania, Italy*

Abstract

We characterized SnO_2:F/p-type a-Si:H heterojunctions by current-voltage (I-V) and capacitance-voltage (C-V) measurements at room temperature to determine the junction parameters. Samples with circular geometry and different diameters were characterized. The current scales with the junction area, and the current density J as a function of the voltage V is a slightly asymmetric curve with a super-linear behaviour (cubic law) for high voltages. Using a transmission line model valid for devices with circular geometry, we studied the effects of the SnO_2:F resistivity on the measured capacitance when the SnO_2:F layer works as an electrical contact. The measured C-V curve allows us to determine junction parameters as doping of p-type a-Si:H, built-in potential and depletion width for the heterojunction with the smallest diameters, demonstrating that for these samples the TCO effects can be neglected. We compared theoretical and measured data to explain qualitatively the transport mechanism in this heterojunction.

Keywords: amorphous silicon; TCO; SnO_2:F; capacitance; heterojunction;

1. Introduction

The thin-film hydrogenated amorphous silicon (a-Si:H) solar cells are attractive for photovoltaic applications and for cheap productions because amorphous silicon is a low cost material. In an a-Si:H p-i-n solar cell a transparent conductive oxide (TCO) is used as electrical contact on the top and bottom of the solar cell. The TCOs are usually degenerate n-type semiconductors and the most used are SnO_2 and ZnO. In a solar cell there are two critical interfaces that are TCO/p-type and n-type/TCO, but the most critical one is the former because it is the window layer. Many authors have studied experimentally [1,2] and by computer modelling [3,4], the TCO/p-type a-Si:H interface, but the transport mechanism and the band diagram are not well modeled and understood. Usually, this interface is treated as a Schottky or ohmic contact. Moreover, in capacitance studies the impact of the TCO on the measured admittance is usually neglected, because it is treated as a perfect conductor. The impact of the TCO in a

* Corresponding author. Tel.: +3909123899026; fax: +3909123860815.
E-mail address: gcannella@difter.unipa.it

1876-6102
doi:10.1016/j.egypro.2011.01.009

solar cell was studied in [5], where it is shown that the losses in the TCO layer influence the measured capacitance of the pin solar cells due to the distributed resistance of the TCO.

In this work we investigate the SnO_2:F/p-type a-Si:H heterojunction with the final goal of understanding the transport mechanism and the energy band diagram of the heterojunction. We performed electrical characterization by measuring the J-V curves to investigate the transport mechanism and the C-V curves to extract some junction parameters. We propose a transmission line model to take into account the impact of distributed resistance of the SnO_2:F layer on the measured admittance. The measured admittance depends on the resistivity of the TCO layer and on the heterojunction admittance. This model, valid for devices with circular geometry as those we characterized, allows us to validate the correct values of the measured capacitance and to extract correctly the junction parameters of the heterojunction.

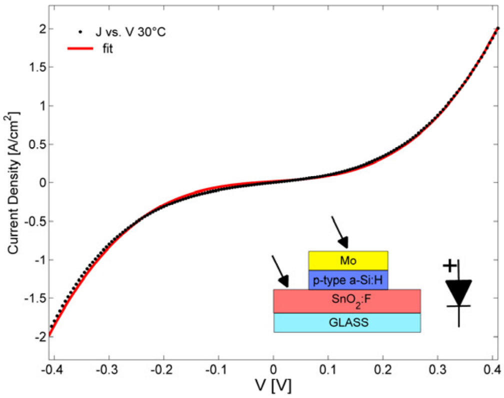

Fig. 1 Measured J-V curve (black) of the heterojunction SnO_2:F/p-type a-Si:H at 30°C for 200 μm diameter. In red the fitting curve with a cubic law ($J = a \cdot V^3 + b \cdot V$) of the measured J-V. In the bottom the schematic and the diode configuration of the devices under test is shown. The positive bias is applied to Molybdenum.

2. Materials and Methods

We characterized SnO_2:F/p-type a-Si:H heterojunction devices realized by STMicroelectronics (Catania, Italy) by plasma-enhanced chemical vapour deposition (PECVD) of SiH_4 and TMB with a ratio B/SiH_4=1% at low temperature onto an AGC ASAHI GLASS substrate consisting in a 1 *mm* thick glass covered with an 800 *nm* thick SnO_2:F film. The geometries were circles, with the following diameters: 200, 400, 800, 1600, 3200, 6400 μm. An 800 *nm* thick molybdenum metallization was deposited by sputtering on a 20 *nm* thick p-type a-Si:H layer. The structure is shown in the inset of Fig.1.

To extract the sheet resistance of the p-type a-Si:H material *ad hoc* samples were realized. In particular, 1000, 100, and 20 *nm* thick p-type a-Si:H films were deposited on silicon substrates covered with a 0.9 μm SiO_2 layer. We characterized the heterojunction by measuring the current density versus voltage (J-V) curves, using four-point probe technique and Keithley 236 as source measure unit. We performed also admittance measurements using an Agilent 4980A LCR meter with four terminal (4T) configuration. The admittance measurements were performed in the frequency range [200 *Hz* to 2 *MHz*], with 30 *mV* AC oscillator amplitude. The temperature is controlled by a Peltier cell with a thermocouple in direct contact to the SnO_2:F. All measurements were taken in dark, at 30°C and in the voltage ranges [–0.4 +0.4] V .

The film sheet resistance of the p-type a-Si:H was measured using the four-point probe technique under vacuum, in dark and at different temperature (300 to 600 K). The temperature dependence of the sheet resistance R_{sh} was measured for constant rates (dT/dt). During the measurement the temperature was controlled and monitored by using an MMR K-20 temperature controller and a Joule-Thompson refrigerator, and the sample temperature was measured by a thermocouple in direct contact to the sample backside.

3. The impact of the TCO on the capacitance measurements

In a solar cell the resistivity of the TCO layer, which is about two orders of magnitude higher than that of a metal, can affect the capacitance measurements performed on the solar cell, when the metallization used for the electrical contact does not cover the whole area of the device. In [5] it was shown this effect in pin a-Si:H thin film solar cells and a transmission-line model was proposed, valid for solar cells with strip geometry. This model allows to estimate the critical geometrical size of solar cells over which the capacitance measurements are sensitive to the TCO resistivity and its relation with the probe frequency, the TCO resistivity and the lumped parasitic series resistance. Usually, the impact of the TCO increases when both the lenght of the TCO strip and the frequency of the AC signal used for the capacitance measurements increase.

In our case, the heterojunction has a metal contact on one side and the TCO on the other side, thus when the devices are contacted by the probe tips on the TCO, the resistivity losses in the TCO layer can alter the value of the measured junction capacitance. Therefore, in order to quantify the effect of the TCO on the capacitance measurements in the investigated devices, we propose an analytical model that is valid for devices with a circular geometry. We model the circular structure as a cylinder of radius *b* composed by the TCO layer of height *t* and sheet resistance R_{sh} and by the heterojunction with admittance Y_j (S/cm^2). The metal circle (the probe tip) of radius *a*, covers the top of the TCO layer. The elementary cell of the transmission line is the cylinder of internal and external radius *r* and *r+dr* respectively, and it is modeled with the series resistance per length unit $R_{sh}/2\pi r$ (Ωcm), due the TCO layer, and the parallel conductance per length unit $Y_j 2\pi r$ (S/cm) of the heterojunction.

By solving Telegrapher's equations we obtain the differential equation for the voltage $V(r)$ along the TCO layer $V'' + V'/r - \gamma^2 V = 0$, where $\gamma = \sqrt{Y_j R_{sh}}$ (cm^{-1}), under appropriate boundary conditions. In the investigated structures we can consider the lateral current density J_L flowing into the TCO and the transverse current J_T flowing into heterojunction. It is the lateral current which causes the voltage drop along the direction *r* due to the TCO resistivity, $dV/dr = -\rho_{TCO} J_L$. Along the metal circle of radius *a* the voltage is constant and equal to the voltage of LCR meter V_0. The lateral current at *r=b* is null. Hence, the boundary conditions for the differential equation are $V(a) = V(0)$ and $dV/dr|_{r=b} = 0$. In order to calculate the measured admittance Y_{meas} we consider that the whole current I_0 going from the LCR to the probe is the sum of the transverse current flowing into the circle of radius *a* and the lateral current J_L, i.e. $I_0 = J_L(a)2\pi a + J_T \pi a^2$, with $J_T = Y_j V_0$.

By combining the solutions of the differential equation with the previous conditions we obtain the following expression of the measured admittance of the heterojunction with circular structure:

$$Y_{meas} = Y_j \left[\left(\frac{a}{b} \right)^2 + \frac{2a}{b^2 \gamma} \frac{I_1(\gamma b)K_1(\gamma a) - I_1(\gamma a)K_1(\gamma b)}{I_0(\gamma a)K_1(\gamma b) + I_1(\gamma b)K_0(\gamma a)} \right] \qquad \textit{(eq. 1)}$$

where I_n and K_n are the modified Bessel functions and $a \le b$. It is immediate to prove that when the metal contact covers the whole area of the TCO layer, i.e. *a=b*, it results $Y_{meas} = Y_j$. When $\gamma b < 1$, i.e. the width of the devices is less than the characteristic length $1/\gamma$, the term in square brackets of *eq.1* approaches to 1, and the measured admittance is equal to that of the heterojunction. Conversely, when $b > 1/\gamma$ this term is lower than 1 and approaches to zero when γb increases. If the heterojunction is a capacitance C_j without losses the characteristic length is $\sqrt{1/\omega C_j R_{sh}}$, which decreases with the frequency and the resistivity of the TCO layer. Thus, when $b > 1/\gamma$ the measured capacitance drops comparing to that of the junction, due to the TCO working as an electrode. With this model we can estimate the effect on the measured capacitance caused by the resistivity of the TCO layers.

4. Measurements and Results

Firstly, we performed sheet resistance measurements of the SnO_2:F material with the four-point probe method. The measured sheet resistance of the SnO_2:F is above 8.8 (Ω/μ). To determine the doping density we used the relation $N_D = 1/(q\mu R_{sh} t)$ and assuming a value of $30\,cm^2/Vs$ for the electron mobility [3], we obtained $N_D = 2.9 \cdot 10^{20}\,cm^{-3}$. Furthermore, we extracted the resistivity activation energy of the p-type a-Si:H material. The sheet resistance R_{sh} of the samples evolves as a function of the temperature T according to $R_{Sh} = R_0 \exp(E_A/kT)$. Where R_0 is the measured resistance at 300 *K* and *k* is the Boltzmann constant. The measured activation energy of the p-type a-Si:H was 0.38 *eV* for all thicknesses used and the resistivity at room temperature was $2 \cdot 10^4\,\Omega cm$.

The J-V curves of the SnO_2:F/p-type a-Si:H heterojunction at 30°C are slightly asymmetrical and follow a cubic law: $J = aV^3 + bV$, as shown in Fig.1. In this structure there are two junctions: Mo/p-type a-Si:H and p-type a-Si:H/SnO_2:F. The Mo/p-type a-Si:H junction can be considered as an ohmic contact, because the current for positive bias voltage is slightly greater than that for negative bias. The equivalent diode is also shown in Fig.1.

We verified that the J-V curves do not change with the radius for the devices with diameter less than 800 μm. For a sample with a diameter of $1600 \mu m$, the effects of the leakage and of the TCO resistivity become relevant. In order to investigate the small signal behaviour of the investigated heterojunctions, we performed impedance measurements. The analysis of the impedance was necessary to correctly implement the C-V intercept method, which we used to determine the built in voltage V_{bi}, the depletion width W and the semiconductor doping N_A .

In Fig. 2 the modulus and the phase of the impedance versus frequencies at V=0V and at different diameters are shown. The impedance shows the same trend in the linear region of the J-V curve that is an increase of the resistance (decreasing of the phase with the diameters). The equivalent circuit of the heterojunction at fixed voltage consists on a parallel conductance G and a capacitance C_j . The capacitance of the heterojunction was measured at 1 *MHz* and for different radius b of the heterojunctions. In Fig. 3 the values of the measured capacitance (circle) at 1 *MHz* and at different diameters of the devices under test are shown. We have chosen to measure the C-V at 1 *MHz* because at a such high frequency the traps do not respond to the AC signal, hence the contribution of traps and interface states to the capacitance can be neglected. Moreover, at 1 *MHz* the capacitance could be extracted with more precision respect to that at lower frequency. But at this high frequency the impact of the TCO could be significant in the capacitance measurements. Thus it was necessary to test the impact of the TCO on the admittance measurements using the transmission line model previously presented. Therefore, we measured the capacitance of the devices with different radii and simulated the results by using *eq.1*. In the admittance measurements we used the four-point probe (Kelvin) connection, thus the voltage drop between the force and sense terminal due to the contact resistances with the tips were eliminated. The use of the Kelvin connection damps the impact of the TCO, because it increases the value of the radius a, which is approximately equal to the distance between the probes (about one a hundred microns). In Fig. 3 the comparison between the measured (circle) and the modeled (continuous line) capacitance at zero bias voltage, at 30°C and for different diameters is shown. We note that the value of the measured capacitance drops when the diameter of the device increases, and the model in *eq.1* predicts this behaviour as seen in continuous line in Fig. 3. In fact, when the diameters of the circular pad is 800 μm the capacitance begins to decrease.

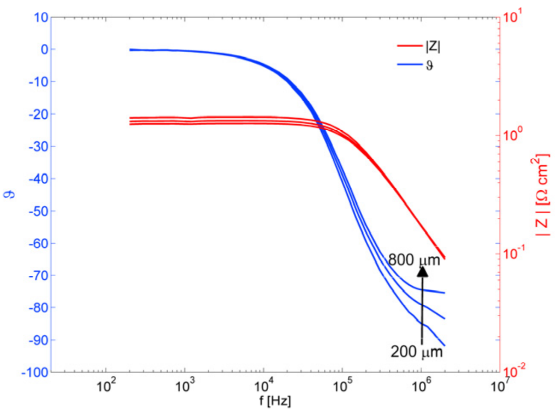

Fig. 2 Phase (blue) and modulus (red) of the measured impedance for different diameters and frequencies at T=30°C.

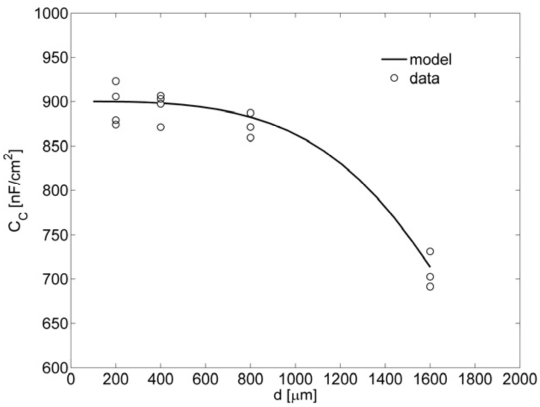

Fig. 3 Comparison between modeled and measured capacitance at 1 *MHz*, at T=30°C and for different diameters *d*.

The transmission line model ensures that the measured values of capacitance are not affected by the resistivity of the TCO for diameters less than the characteristic length $1/\gamma \cong 500\ \mu m$. Therefore, using the samples with diameter of 200 μm for capacitance measurements, the TCO effects are negligible and the measured capacitance coincides with that of the junction. After testing the TCO effect in the capacitance measurements, we were able to perform the C-V intercept method at zero bias voltages because the capacitance was governed by junction capacitance.

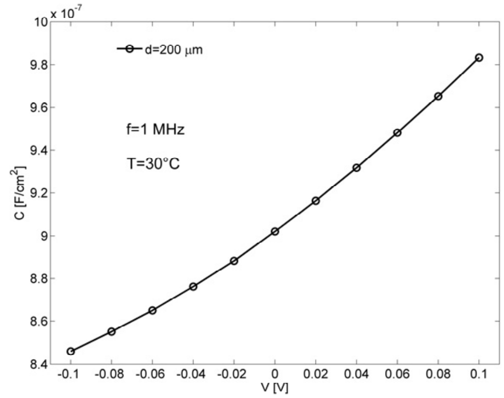

Fig. 4 Example of measured C-V curves with 200 μm of diameter at f=1 *MHz* and T=30°C

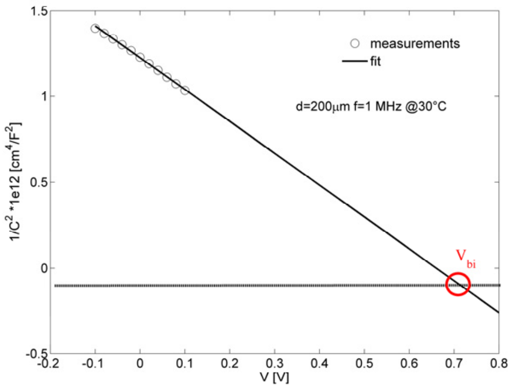

Fig. 5 Example C^{-2}-V curve used for the C-V intercept method to determine the junction parameters.

In fig. 4 the C-V curve in the linear region for samples with 200 μm diameter and at room temperature is shown. If the interface charge influences the heterojunction, the C-V curve decreases with the bias voltage [5]. In our case, the C-V curves increase monotonically, hence the contribution of the interface charges in C-V curves can be neglected.

In fig. 5 an example of the C^{-2}-V is shown. It has a linear behaviour so the deep traps do not play an important role in this heterojunction [6]. In this case the intercept voltage V_{int} of C^{-2}-V plot is equal to the total built-in potential V_{bi} of the heterojunction when the doping level is known, if the Gummel-Scharfetter correction [7] can be neglected: $V_{\text{int}} \cong V_{b2} + V_{b1} \approx V_{bi}$ and for abrupt heterojunctions. By linear fitting of the C^{-2}-V curves, we can extract the intercept voltage V_{int}, the doping of p-type a-Si:H layer N_A and the depletion width W [8]. The built-in potential is close to the difference between the work functions of SnO_2:F (4.8 *eV*) and of the p-type a-Si:H film. The latter is equal to the sum of the a-Si:H affinity (3.9 *eV*) and the distance between conduction band and Fermi level (difference between energy gap and measured activation energy: 1.87-0.38=1.49 *V*). This implies an expected V_{bi} of 0.59 *V*. The measured V_{bi} is 0.66 eV, that is, quite close to the expected value (0.59 *eV*). The difference between extracted and expected value can depend on the interface traps, probably acceptor interface charges [4]. The depletion width is 11.7 nm and the doping of p-type a-Si:H is $6.4 \cdot 10^{18}\ cm^{-3}$. The found values are consistent and allow to describe the heterojunction between SnO_2:F and a-Si:H.

5. Discussions and conclusions

This work is a preliminary study of the J-V and C-V curves at room temperature for the SnO_2:F/p-type a-Si:H heterojunction to extract the junction parameters. In literature there were some experimental studies on similar heterojunctions, [1,2], but in both works the heterojunction was considered as a Schottky contact governed by thermionic emission, without considering other possible transport mechanisms. They also used different measurement methods as J-V under illumination and the pulsed laser-induced transient photopotential technique. In this work we performed direct electrical measurements as C-V and J-V to determine the junction parameters and we demonstrated that the investigated heterojunction is not a Schottky contact, because the J-V curve is slightly asymmetrical and it is not rectifying. Moreover, the J-V curves do not follow exponential law in any range of voltage bias, thus we can also rule out diffusion and recombination as possible principal transport mechanisms. By using the expressions valid for abrupt heterojunction without interface traps and by using the extracted doping of the SnO_2:F and p-type a-Si:H i.e. $N_D = 2.9 \cdot 10^{20} cm^{-3}$ and $N_A = 6.4 \cdot 10^{18}\ cm^{-3}$ respectively, we can estimate the depletion width *W* and the barrier height V_b in both materials [9], indicating with 1 the parameters of the SnO_2:F and with 2 of the p-type a-Si:H:

$$W_1 = \left[\left(\frac{2\varepsilon_1\varepsilon_2 V_{bi}}{q}\right)\cdot\left(\frac{N_A}{N_D(N_A\varepsilon_2 + N_D\varepsilon_1)}\right)\right]^{1/2} \qquad W_2 = \left[\left(\frac{2\varepsilon_1\varepsilon_2 V_{bi}}{q}\right)\cdot\left(\frac{N_D}{N_A(N_A\varepsilon_2 + N_D\varepsilon_1)}\right)\right]^{1/2} \qquad (eq.\ 2)$$

$$V_{b1} = \frac{qN_D W_2^2}{2\varepsilon_1} \qquad V_{b2} = \frac{qN_A W_2^2}{2\varepsilon_2},$$

where ε is the dielectric constant and q is the electronic charge. Therefore, we can estimate the band bending and the depletion width in both semiconductors: V_{b1}=0.07 *eV* and W_1=1 *nm* in SnO_2:F, and V_{b2}=0.60 and W_2=10.7 nm in the a-Si:H. Hence, the barrier seen by the holes in the p-type a-Si:H is quite high and tunnel via localized states in the p-type a-Si:H and subsequent recombination [10] could explain the transport through this interface. We are currently performing further analysis on these aspects.

In conclusion, we determined a sheet resistance of the SnO_2:F of 8.8 Ω/□ and an activation energy of p-type a-Si:H of 0.38 *eV*. We modelled the effect of the TCO considering a circular geometry for the devices under test. We demonstrated that for diameters greater than the characteristic length (500μm) the effect of the TCO became important in the measured capacitance at zero voltage bias and 1 *MHz*. We performed measurements only for diameters less than 500 μm to neglect the TCO effect in the devices under test. We performed also J-V and C-V measurements at room temperature to extract the junction parameters of the devices and we demonstrated that the measured curves depended mainly on the SnO_2:F/p-type a-Si:H heterojunction. The data were reproducible and we characterized the junction using the C-V intercept method. We found a depletion width of the junction of 11.7 *nm*, a built in potential of 0.66 *eV* similar to expected value of 0.59 *eV* and a p-type a-Si:H doping of $6.4 \cdot 10^{18}\ cm^{-3}$. We estimated the depletion width and the band bending in both semiconductors. We are now performing further experimental analyses to better clarify the charge transport mechanisms.

6. Acknowledgments

This work has been carried out with the partial support by the University of Palermo through the ex-60% funds and by STMicroelectronics. We gratefully acknowledge the team of STMicroelectronics (S. Coffa, S. Di Marco, A. Grasso, S. Ravesi, N. Sparta) for support on the research development.

7. References

[1] F. Sanchez Sinencio and R. Williams, "Barrier at the interface between amorphous silicon and transparent oxides and its influences on solar cell performance", J. Appl. Phys, 54 (5), May 1983, 2757.

[2] K. Itoh, H. Matsumoto, T. Kobata, A. Fujishima, O. Nakamura and K. Fukui, "Determining height of a leaky Schottky barrier existing in the junction between SnO_2 and highly doped p-type amorphous SiC by using the pulsed laser-induced transient photopotential technique", Appl. Phys. Letter, 51 (1987) 1685.

[3] F. Smole, M. Topic and J. Furlan ,"Analysis of the TCO/p(a-Si:C:H) heterojunction and its influence on p-i-n a-Si:H solar cell performance", J. of Non-Crystalline Solids,194 (1996), 312-318.

[4] J.S.C. Prentice, "The effect of surface states at the SnO_2/p-a-Si:H interface", J. of Non Crystalline solids 262 (2000) 99-105.

[5] F. Principato, G. Cannella, M. Foti and S. Lombardo, "Impact of transparent conductive oxide on the admittance of thin film solar cells" Solid State Electronics, 54, (2010), 1284.

[6] H. Kromer, "Heterostructures devices: a device physicist looks at interface", SurfaceScience 132, (1983), 543.

[7] H.K. Gummel and D.L. Scharfetter, "Depletion layer capacitance of p^+n step junctions" J. Appl. Phys. 38, (1967), 2148.
[8] S.M. Sze, "Physics of semiconductor devices", 2nd edition, Wiley Interscience, 1981.
[9] J. Singh and U.K. Mishra, "Semiconductor devices and physics" Springer.
[10] M. Vukadinović, F. Smole, M. Topič, R.E.I. Schropp and F.A. Rubinelli "Transport in tunneling recombination junctions: a combined computer simulation study", J. of Appl. Phys. 96, iss.12, (2004), 7289.