

# INVESTIGATION OF INTERFACE TRAPS OF MOS STRUCTURES WITH ULTRATHIN SiO<sub>2</sub> LAYERS USING ACOUSTOELECTRIC RESPONSE

Peter HOCKICKO, Peter SIDOR, Peter BURY

Department of Physics, Faculty of Electrical Engineering, University of Žilina,  
Veľký diel, 010 26 Žilina, Slovak Republic, tel.: +421 41 513 2364, mail:hockicko@fyzika.uniza.sk

## ABSTRACT

The interfaces of MOS (metal–oxide–semiconductor) structures with ultrathin silicon dioxide (SiO<sub>2</sub>) layers formed on Si substrate with nitric acid have been investigated using both acoustic deep-level transient spectroscopy (A-DLTS) and  $U_{ac}^0(V_G)$  dependences to characterize the interface states. The methods are based on the acoustoelectric response signal (ARS) observed on the interface when hf longitudinal wave propagates through the structures. The ARS is extremely sensitive to external conditions and reflects any changes in the charge distribution connected also with charged traps. The MOS structures were investigated using acoustic techniques to find the interface states and their distribution after post-oxidation annealing (POA) and/or post-metallization annealing (PMA) treatment on the interface-state occurrence and distribution. The evident decreases of interface states and shift of their activation energies in the structures with PMA treatment in comparison with POA treatment were observed in the investigated structures. The activation energies and some other parameters of traps at the insulator – semiconductor interface were determined.

**Keywords:** interface states, MOS structures, semiconductor-insulator interfaces, acoustic DLTS

## 1. INTRODUCTION

The interface states in metal – oxide – semiconductor (MOS) structures have been investigated for more than thirty years using many useful experimental techniques. The A-DLTS version is high-frequency ultrasonic method based on analysis of acoustoelectric response signal (ARS) produced by MOS structure after bias voltage steps is applied to the structure at various temperatures that reflects relaxation processes in both semiconductor and interface layer. It was namely found, that the ARS strongly depends on the bias voltage applied to the structure and reflects any changes in the space charge distribution due to the external condition changes [1]. The measurement of ARS as a function of the gate bias voltage can be useful method determining the energy distribution through the energy band gap [2].

Using the chemical SiO<sub>2</sub> layers formed in HNO<sub>3</sub> (nitric acid oxidation of Si - NAOS), the formation of ultrathin SiO<sub>2</sub> layers with a leakage current density much lower than those of thermally grown SiO<sub>2</sub> layers, or layers prepared by a different chemical oxidation procedure with the same thickness [3], can be performed. The leakage current density and consequently the interface state density can be decreased by a post oxidation annealing (POA) treatment in a nitrogen atmosphere [4] and/or a post-metallization annealing (PMA) treatment in a hydrogen atmosphere [5]. The POA and PMA treatment can also eliminate interface states and decrease the leakage current density of MOS diodes. Acoustic deep-level transient spectroscopy (A-DLTS) as well as  $U_{ac}(V_G)$  characteristics are used in present contribution for the study of ultrathin NAOS SiO<sub>2</sub>/Si interfaces to clarify the role of annealing treatment on the interface states occurrence and distribution.

## 2. THEORETICAL PRINCIPLES

The basic principle of A-DLTS technique consists in utilization of the ARS produced by MOS structure

interface when a high frequency acoustic longitudinal wave traverses the structure. The amplitude of the acoustoelectric response can be written in the form

$$U_{ac}^0(V_G) = K |Q(\varphi_s(V_G))|, \quad (1)$$

where  $K$  is the experimental constant,  $Q$  is the density of the accumulated charge,  $\varphi_s$  is the surface potential across the semiconductor and  $V_G$  is gate bias voltage.

After an injection pulse has been applied to the semiconductor structure the amplitude of ARS follows the accumulated charge behaviour over the capacitance, so that the ARS is proportion to the nonequilibrium carrier density  $\Delta n$  [6]

$$\Delta n(t) = \Delta n_{t0} \exp\left(-\frac{t}{\tau}\right), \quad (2)$$

where  $\Delta n_{t0}$  represents the variation in trap occupancy due to the acoustoelectric effect and  $\tau$  is the time constant associated with the release of the carrier from deep centers (relaxation time).

The measured acoustoelectric response signal amplitude for the discrete level can be then given by

$$U_{ac}^0(t) = U_0 \exp\left(-\frac{t}{\tau}\right). \quad (3)$$

The reciprocal value of  $\tau$  gives the emission rate which for electrons can be expressed by the relation

$$\tau^{-1} = \gamma_n \sigma_n T^2 \exp\left(-\frac{E_a}{k T}\right), \quad (4)$$

where  $\gamma_n$  is constant,  $\sigma_n$  is the capture cross section,  $E_a = E_c - E_T$  is the trap activation energy related to the bottom of conduction band,  $k$  is Boltzman's constant.

Using the A-DLTS technique based on computer-evaluated isothermal transients and correlation procedure with higher order on-line filters and rectangular weighting function [6], the activation energies  $E_a$  and corresponding capture cross-section  $\sigma_n$  of traps can be determined from Arrhenius type dependence  $\ln(\tau_{max} T_{max}^2)$  versus  $1/T_{max}$ .

The dependence of ARS amplitude on the gate bias voltage  $V_G$  applied to the ideal MOS structure can be described by Eq. 1. In general, gate bias voltage  $V_G$  relates to the surface potential  $\phi_s$  as in the following equation

$$V_G - V_{FB} = -\frac{Q(\phi_s)}{C_{ox}} + \phi_s, \quad (5)$$

where  $V_{FB}$  is the flat band voltage,  $C_{ox}$  is the oxide capacitance.

To determine the energy distribution of interface traps it is necessary to know the dependence of surface potential on the gate bias voltage  $\phi_s = f(V_G)$  for the ideal MOS structure. This dependence can be obtained by numerical solution of the Eq. 5 using model which suggests that the density of the accumulated charge in the Eq. 5 can be written for the n-MOS structure as

$$Q(\phi_s) = A \sqrt{\exp\left(\frac{q\phi_s}{kT}\right) - \frac{q\phi_s}{kT} - 1 + \frac{n_i}{N_D} \left(\exp\left(-\frac{q\phi_s}{kT}\right) + \frac{q\phi_s}{kT} - 1\right)} \quad (6)$$

where

$$A = \pm \frac{2kT\epsilon_0\epsilon_s}{qL_D} \quad (7)$$

and  $T$  is the thermodynamic temperature,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_s$  is the dielectric constant of the semiconductor,  $q$  is the elementary charge,  $L_D$  is Debye's length,  $N_D$  is the concentration of the donors,  $n_i$  is the intrinsic concentration in the semiconductor, the sign plus is in the Eq. 7 for the depletion or inversion state and the sign minus for the accumulation state.

If we substitute on the right side of the Eq. 1 the dependences  $Q = f(\phi_s(V_G))$  using considered model, we can obtain the dependence of the ARS on the gate bias voltage for an ideal MOS structure. Now, when we know the both ideal and real voltage dependence of the ARS of the investigated MOS structure, we can determine the energy distribution of the interface traps. The traps cause the shift of the measured curve against the ideal curve by the value  $\Delta V_G(\phi_s)$  that is the function of the surface potential. Following the knowledge of the dependence  $\Delta V_G(\phi_s)$  the density of charge of interface traps can be calculated

$$Q_{it}(\phi_s) = C_{ox} \Delta V_G(\phi_s). \quad (8)$$

This dependence is very important for determination of the energy distribution of interface traps. The energy distribution of the interface traps can be expressed using the equation

$$D_{it} = \frac{1}{q^2} \left| \frac{\partial Q_{it}(\phi_s)}{\partial \phi_s} \right|, \quad (9)$$

where  $D_{it}$  is the interface traps density.

The energy level  $E$  in the band gap of the semiconductor, corresponding to  $D_{it}(E)$ , can be calculated from the equation

$$E = E_v + \frac{E_g}{2} + q\phi_s \pm kT \ln\left(\frac{N_{D,A}}{n_i}\right), \quad (10)$$

where  $E_v$  is the maximum of the semiconductor valence band,  $E_g$  is the semiconductor band gap,  $N_{D,A}$  is the concentration of donors or acceptors, the plus sign is in the Eq. 10 for the n-MOS and the minus sign for the p-MOS structure.

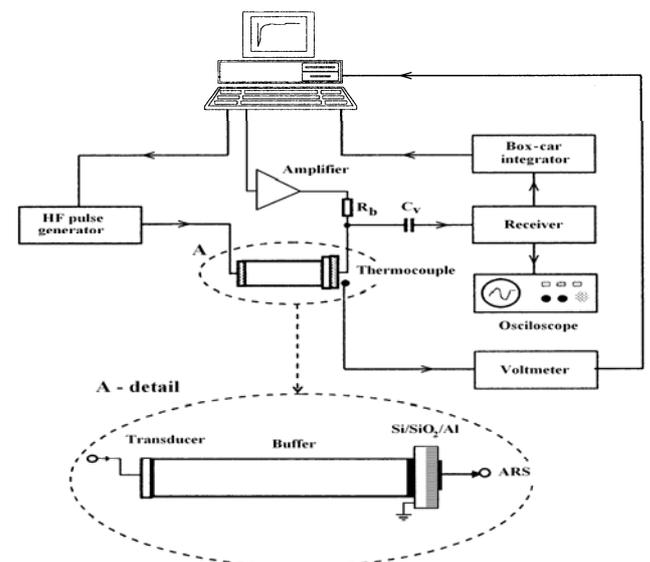
Another method for determining the basic parameters of traps at the insulator – semiconductor interface is the modelling of measured spectra [7]. For discrete levels we can model the measured A-DLTS spectra for the various rate windows  $\Delta t$  and the activation energies  $E_a$  determined from this modelled spectra expressed by the relation

$$\Delta U_{ac}^0(T) = \sum_{j=1}^n U_{j0} \left( \exp\left(-\frac{t_1}{\tau_j}\right) - \exp\left(-\frac{t_2}{\tau_j}\right) \right) \quad (11)$$

can be compared with the activation energies calculated from Arrhenius plots.

### 3. EXPERIMENTAL

A block diagram of the experimental arrangement of the A-DLTS technique is shown in Fig. 1. The computer system was used to trigger the apparatus - Pulse Modulator and Receiver - MATEC 7700, to generate excitation bias pulses as well as to record and evaluate the isothermal transient of the ARS. A longitudinal acoustic wave of frequency 13.2 MHz was generated using a LiNbO<sub>3</sub> transducer in the arrangement illustrated in the A-detail. The ARS produced by the MOS structure, after detection in the SRS Gated Integrator and Box-car



**Fig. 1** Block diagram of the experimental setup for A-DLTS measurement. The sample configuration is illustrated in A-detail

Averager, was then recorded and stored by computer. The  $U_{ac}(V_G)$  dependences were measured under the linear rise at the external voltage  $V_G$ .

Investigated Si MOS structures were fabricated from phosphorus doped Si (100) wafers with 10 Ωcm resistivity. After cleaning the wafers and etching with dilute hydrofluoric acid they were immersed in a nitric acid aqueous solution of various concentrations (changing from 53% to 68%) at temperatures (110-120°C) for different reaction times (changing from 3.5 up to 10 hours). The MOS structures of different oxide layer thickness (2.7 – 9.2 nm) were prepared by this way [8]. After rinsing with ultrapure water the wafers were divided into several parts. One part of the wafers was treated by POA in nitrogen at 250°C for 1 h. Then aluminium (Al) dots of 0.15 and 0.30 mm diameter were formed on all parts of prepared wafers, resulting in Al/SiO<sub>2</sub>/Si MOS diodes. For other wafers, PMA treatment occurred after Al electrodes were evaporated at 250°C in hydrogen atmosphere for 1h.

4. RESULTS

Fig. 2 shows the representative A-DLTS spectra of two MOS structures, sample No. 5 exposed to both POA and PMA treatments. The illustrated spectra that contain only one peak, corresponding to one interface state, were measured at reverse bias  $V_G = -0.5$  V with pulse voltage  $\Delta V_G = 1.2$  V and the same time constant. The activation energies and the corresponding capture cross-sections were determined from the Arrhenius plots constructed for individual peaks. The obtained activation energy related to the bottom of conduction band  $E_a = E_c - E_T = 0.42$  eV with the cross section  $4.52 \times 10^{-16}$  cm<sup>2</sup> for sample POA and  $E_a = 0.75$  eV with the cross section  $4.8 \times 10^{-9}$  cm<sup>2</sup> for sample PMA (Fig. 3). Using the Eq. 11 for the discrete level we simulated the main peak of measured spectra of the sample POA (Fig. 2) for the point  $t_1 = 15$  ms and  $t_2 = 30$  ms. We found the energy level  $E_a' = 0.44$  eV (Fig. 4), which is very close to the activation energy calculated from Arrhenius plot (Fig. 3).

The A-DLTS spectra of PMA structure definitely indicate the lower concentration of interface states compared with POA structure represented by smaller or even an undetected A-DLTS peak. Except for a lower concentration of interface states in the structures with PMA compared with POA structures, the shift of their activation energies above or below the midgap was observed.

This indicates that the same interaction of Si dangling bonds with hydrogen, Si, or oxygen atoms in the SiO<sub>2</sub> layer can occur during the PMA treatment, as well as the reaction between the Al atoms and SiO<sub>2</sub>, producing the Al<sub>2</sub>O<sub>3</sub> layer.

The measured and ideal curves of the ARS dependence on the gate bias voltage for representative sample POA are illustrated in Fig. 5. The corresponding energy distribution is illustrated in Fig. 6.

From this picture we can observe that in the middle of band gap is broad peak of interface traps density. Maximum of this peak is located 0.42 eV from the bottom of conduction band what agree with A-DLTS results (Fig. 3).

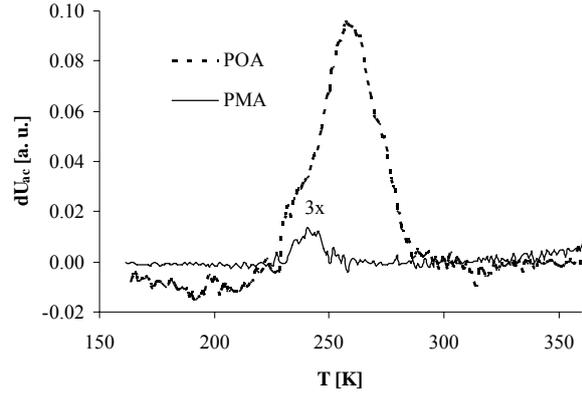


Fig. 2 A-DLTS spectra of the samples SiO<sub>2</sub>/Si structures POA and PMA treated (3.8 nm SiO<sub>2</sub>) for the same relaxation time ( $\tau = 43.6$  ms) at  $V_G = -0.5$  V and  $\Delta V_G = 1.2$  V

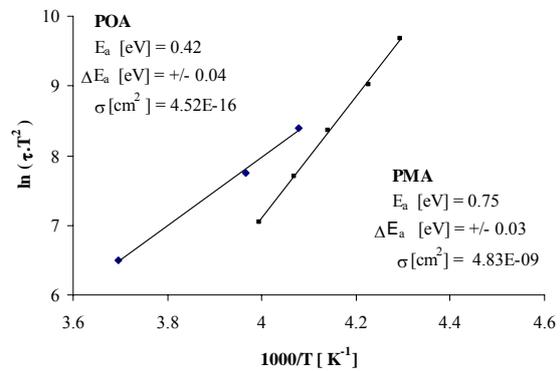


Fig. 3 Arrhenius plot constructed from the positions of the peak maxima of the A-DLTS spectra illustrated in Fig. 2

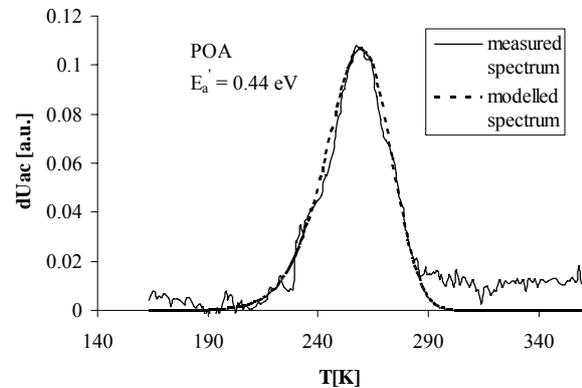


Fig. 4 The simulation peak of A-DLTS spectra of sample POA obtained for the relaxation time 43.6 ms

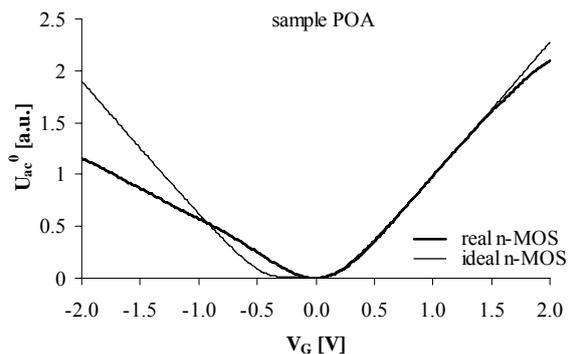


Fig. 5 The measured and ideal voltage dependence of ARS of the sample POA

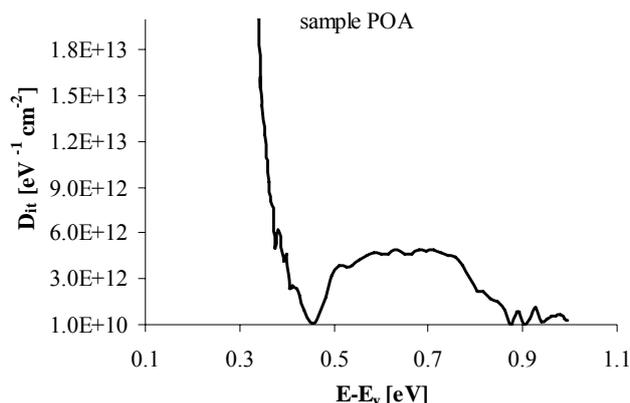


Fig. 6 The energy distribution of the interface traps in the sample POA

## 5. CONCLUSIONS

The SiO<sub>2</sub>/Si structures with SiO<sub>2</sub> layers formed in HNO<sub>3</sub> solutions (NAOS method) in MOS configuration were investigated by acoustical techniques to compare the role of POA and/or PMA treatment. We found some physical parameters of the interface states in Si(n)-SiO<sub>2</sub> MOS structures. Using A-DLTS spectra from Arrhenius plots we identified the activation energies of the deep centers at SiO<sub>2</sub>-Si interface.

The A-DLTS spectra indicated different interface states after the POA treatment, depending on the formation conditions. Using the PMA treatment, the different states compared with POA samples were observed by A-DLTS, confirming the reduction of Si dangling bonds, resulting from the formation of weak bonds with surrounding atoms and definitely with lower concentration.

The determination of the interface traps density based on the measurement of the ARS can be another useful technique characterizing the interface trap density distribution in MOS structures.

## ACKNOWLEDGMENTS

The authors would like to thank prof. H. Kobayashi, assoc. prof. M. Takahashi and Dr. K. Imamura from Institute of Scientific and Industrial Research, Osaka University, Japan for preparation and provision investigated samples and Mr. F. Černobila for technical assistance. This work was financially supported by the R&D operational program Centrum of excellence of power electronics systems and materials for their components, No. OPVaV-2008/2.1/01-SORO, ITMS 26220120003 funded by European Community, VEGA project No. 2/7120/07 and project APVV-0577-07 of the Ministry of Education of the Slovak Republic.

## REFERENCES

- [1] BURY, P. – JAMNICKÝ, I. – ĎURČEK, J.: *Physica Status Solidi* (a) 126, (1991) 151.
- [2] BURY, P. – JAMNICKÝ, I.: *Acta Phys. Slovaca* 46, (1996) 693.

- [3] KOBAYASHI, H. – ASUHA, A. – MAIDO, O. – TAKAHASHI, M. – IWASA, M.: *J. Appl. Phys.* 94, (2003) 7328.
- [4] ASUHA, A. – KOBAYASHI, T. – TAKAHASHI, M. – IWASA, M. – KOBAYASHI, H.: *Surf. Sci.* 547, (2003) 275.
- [5] ASUHA, A. – IMAI, S. – TAKAHASHI, M. – KOBAYASHI, H.: *Appl. Phys. Lett.* 85, (2004) 3783.
- [6] BURY, P. – JAMNICKÝ, I. – HOCKICKO, P.: *Communications* No. 2, (2003) 5.
- [7] HOCKICKO, P. – SIDOR, P. – BURY, P. – KÚDELČÍK, J. – JAMNICKÝ, I.: *Advances in Electrical and Electronic Engineering* 7 No. 1-2, (2008) 373.
- [8] BURY, P. – KOBAYASHI, H. – TAKAHASHI, M. – IMAMURA, K. – SIDOR, P. – ČERNOBILA, F.: *Cent. Eur. J. Phys.* 7(2), (2009) 237.

Received March 17, 2010, accepted July 30, 2010

## BIOGRAPHIES

**Peter Hockicko** was born on 8. 2. 1973. In 1996 he graduated (MSc) with distinction at the Faculty of mathematics, physics and informatics at the Comenius University in Bratislava. He defended his PhD in the field of physics of condensed matter and acoustics in 2008; his thesis title was “Study of relaxation processes in matter using acoustic methods“. Since 1999 he has been working as a tutor at the Department of Physics at the Faculty of Electrical Engineering at the University of Žilina. His scientific research focuses on relaxation processes.

**Peter Sidor** was born on 1.11.1975. In 1999 he graduated (MSc) at the Department of Solid State Physics of Faculty of mathematics, physics and informatics CU in Bratislava. Since 2004 he is Ph.D. student at the University of Žilina. Since 2003 he is working as a tutor at the Department of Physics at the Faculty of Electrical Engineering at the University of Žilina.

**Peter Bury** received the M.Sc. in experimental physics in 1972 and PhD. in 1982 at the Faculty of Natural Sciences (Faculty of Mathematics and Physics), Comenius University, Bratislava. Currently he is Professor of Physics of Condensed Matter and Acoustics at Department of Physics, Faculty of Electrical Engineering, Žilina University. The most of his research work was orientated on the study of semiconductors and semiconductor structures using acoustic methods. Formerly he investigated Cr states in GaAs using APR technique, later deep centers in both semiconductor and semiconductor structures using acoustic transient spectroscopy (A-DLTS). Currently he uses methods of acoustic spectroscopy also to study glasses, ferroelectrics and magnetic fluids.