Ultra-shallow nitrogen plasma implantation for ultra-thin silicon oxynitride (SiO$_x$N$_y$) layer formation

Tomasz Bieniek, Romuald B. Beck, Andrzej Jakubowski, and Andrzej Kudła

Abstract— The radiation damage caused by low energy r.f. plasmas has not been, to our knowledge, studied so far in the case of symmetric planar plasma reactors that are usually used for PECVD processes. The reason is that, unlike non-symmetrical RIE reactors, such geometry prevents, basically, high-energy ion bombardment of the substrate. In this work, we present the results of experiments in which we have studied the influence of plasma processing on the state of silicon surface. Very low temperature plasma oxidation has been used as a test of silicon surface condition. The obtained layers were then carefully measured by spectroscopic ellipsometry, allowing not only the thickness to be determined accurately, but also the layer composition to be evaluated. Different plasma types, namely N$_2$, NH$_3$ and Ar, were used in the first stage of the experiment, allowing oxidation behaviour caused by the exposure to those plasma types to be compared in terms of relative differences. It has been clearly proved that even though the PECVD system is believed to be relatively safe in terms of radiation damage, in the case of very thin layer processing (e.g., ultra-thin oxynitride layers) the effects of radiation damage may considerably affect the kinetics of the process and the properties of the formed layers.

Keywords— *MOS technology, plasma processing, shallow implantation, radiation damage.*

1. Introduction

ITRS roadmap [1] forecasts an increase of the packaging density and improvement of the performance of silicon integrated circuits by the reduction of the of gate dielectric thickness, among other factors.

In mixed logic/memory circuits manufactured as a system on a chip, two different thicknesses of dielectric layers are required. The solution the most advanced technologically would be to form both dielectric layers during a single process. This may be possible through the oxidation of a nitrogen-implanted silicon layer, where the oxidation rate depends on the nitrogen implantation dose and profile (e.g., [2, 3]).

The experiments presented in this work are a part of a broader study that examines the possibility of conducting both stages of ultra-thin oxynitride formation (e.g., ultra-shallow nitrogen implantation and silicon oxidation) in one technological reactor.

The important issue here is the possibility of carrying out extremely shallow ion implantation by means of planar r.f. reactors. For the time being planar reactors have been believed to enable very limited bombardment only, especially in the case of symmetrical reactors – used for PECVD process. In non-symmetrical reactors used for reactive ion etching (RIE) the effects of ion bombardment have been employed practically to etch layers, no data or even estimation have, however, been presented (to our knowledge) so far on the depth of implantation and significance of this effect.

Such effects may not only influence the process of layer forming, but also influence their properties.

2. Experimental

In contrast to the methods presented so far in the literature where classical implanters or the ion immersion implantation in plasma (IIIP) method were used to carry out ultra-shallow implantation, in our work we used typical planar r.f. plasma reactors usually applied in PECVD. The processes of plasma implantation of nitrogen and subsequent plasma oxidation are both taking place at a very low temperature 350°C.

The nitrogen N$_2$ and ammonia NH$_3$ plasmas were used in this investigation (stage 1). This allowed the effect of easier dissociation and excitation of ammonia to be compared to that of nitrogen.

The subsequent process of plasma oxidation (stage 2) was carried out in conditions resulting from the studies of plasma oxidation at very low temperatures presented in [4]. The kinetics of oxidation are highly dependent on the state of the silicon surface. The disorder of this region (e.g., amorphisation) obviously results in a higher oxidation rate.

Spectroscopic ellipsometry was used to measure the thickness of the obtained layers. Since either nitrogen or ammonia plasma was used in the first process (stage 1), we could expect some nitride content in the layer – the appropriate optical model had to be incorporated. Our earlier experience has proved that even in the case of low nitride-phase content, we may obtain very good agreement of the EMA model with the spectrum measured by ellipsometer in a very wide range of wavelengths. An example of fitting the EMA model to the real ellipsometric spectrum is shown in Fig. 1. In the EMA model, we included two phases most likely to be present in our layers, namely:

Table 1

Complete matrix of experiments – two-stage processes performed in a PECVD system; the results obtained by means of spectroscopic ellipsometry measurement analysis are also included

| Process name	Oxid. only		50 W Ar		100 W Ar		50 W N$_2$		100 W N$_2$		50 W NH$_3$		100 W NH$_3$	
Stage 1 process														
Gas type			Ar				N$_2$				NH$_3$			
Gas flow [ml/min]			50				50				50			
Pressure [Tr]			0.5				0.5				0.5			
Temperature [°C]			350				350				350			
Process time [min]			5				5				5			
Power [W]			50		100		50		100		50		100	
Stage 2 process														
Power [W]	50		50				50				50			
Gas type	O$_2$		O$_2$				O$_2$				O$_2$			
Gas flow [ml/min]	50		50				50				50			
Pressure [Tr]	0.5		0.5				0.5				0.5			
Temperature [°C]	350		350				350				350			
Process time [min]	2	10	2	10	2	10	2	10	2	10	2	10	2	10
Results of the spectroscopic ellipsometry measurements														
Optical thickness [Å]	44	66	59	91	73	130	36	68	55	171	36	60	32	63
Refractive index (@630 nm)	1.477	1.471	1.488	1.477	1.453	1.460	1.443	1.463	1.509	1.433	1.627	1.542	1.663	1.526
Si$_3$N$_4$ content [%]	–	–	5.92	3.78	0.1	0.64	0.1	1.14	9.98	0.1	31.6	16.1	37.9	13.2
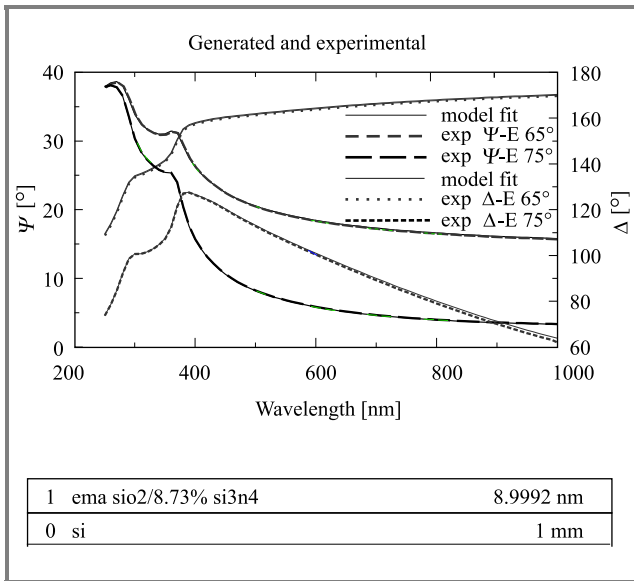
Fig. 1. An example of a fitting of the optical EMA model to measurement data in wide range of wavelength (from 250 nm to 1000 nm) for two incident angles 65° and 75°. Very good agreement allows both layer thickness determination and approximate evaluation of layer composition.

silicon dioxide (SiO$_2$) and silicon nitride (Si$_3$N$_4$), although we could also expect some "optically detected" consequences of the amorphisation of silicon. The fitting of this model to the measured spectrum fitting is very good (low values of mean deviation error) indirectly justifying our choice of phases included in the EMA model.

In order to isolate the impact of amorphisation of the silicon substrate, by implanted nitrogen ions, on the final kinetics of oxidation, reference experiments were done with argon implantation (stage 1) under similar conditions.

The complete set of experiments is presented in Table 1. It should be noted that each experiment was carried out for two process times (2 and 10 minutes) of plasma oxidation (stage 2), and two levels of r.f. power (50 W and 100 W) applied during nitrogen implantation (stage 1). The oxidation process was carried out with the power of r.f. oxygen plasma equal to 50 W.

The independent information about possible consequences of ion collisions with the silicon substrate was obtained from TRIM simulations. They allowed probable profiles of implanted atoms to be evaluated, as well as profiles and densities of the expected damage in the silicon crystal lattice – factors that obviously determine the kinetics of the subsequent process of plasma oxidation of silicon.

3. Results and discussion

The results of all ellipsometric measurements characterising all experiments performed in this study are also included in Table 1.

When looking at the obtained results one can immediately realise that the history (type of plasma process and

r.f. power used at stage 1) does have enormous impact on the final layer thickness and its composition. Basically, one could say that each of the process sets results in different oxide (oxynitride) thickness. However, studying the relative differences can bring more interesting information on the effects that are most probably responsible for those differences.

The undisturbed kinetics of the plasma oxidation process was observed by means of the reference process with oxygen plasma only (stage 2 only). The thickness dependence was comparable to the results obtained in our previous work on plasma oxidation [4]. The difference in the oxide thickness observed in the samples bombarded in argon plasma (stage 1) for both, lower and higher r.f. argon plasma power is clear (see Fig. 2). At the same time, for both oxidation times the obtained oxide layer thickness is higher in the case of samples exposed primarily (during stage 1) to Ar plasma. Furthermore, substantial difference in the obtained thickness is observed between 50 W and 100 W r.f. Ar plasma (see also Fig. 2).
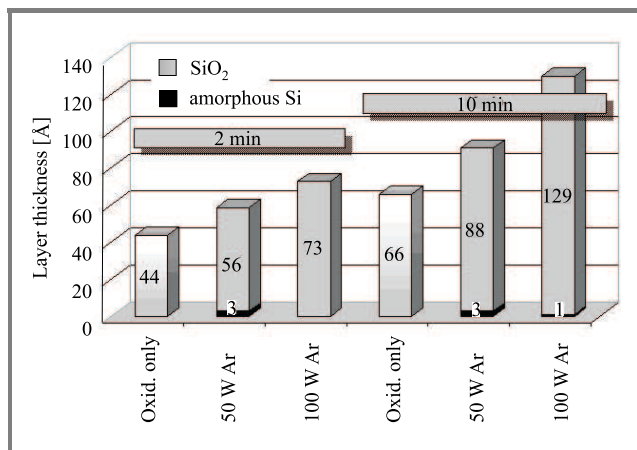

Fig. 2. The total and component-layer thickness (as evaluated using EMA model) of the layers obtained by plasma oxidation of samples exposed to argon plasma. The results of plasma oxidation only are used as a reference.

The observed results seem to be obvious, if we realise that due to chemical passivity of argon the only possible effect of silicon exposure to Ar plasma can be the damage to silicon surface due to energetic Ar ion bombardment. In these conditions the dependence of oxide thickness on r.f. power applied to plasma is simple – the higher the r.f. power, the higher ion bombardment is expected and thus, more damage is done to the silicon substrate. The damage obviously enhances oxide growth, therefore the final oxide thickness is the highest (in this set of experiments) for the process using the higher r.f. power (100 W) of argon plasma during stage 1. We have to keep in mind that, the enhancement of oxidation rate will end as soon as the whole damaged region of the silicon substrate is be consumed by plasma oxidation.

A different situation occurs when nitrogen or ammonia plasmas are used in the stage 1 process (see Fig. 3).

In the case of nitrogen plasma short oxidation time results in lower or slightly greater layer thickness (for lower and higher r.f. plasmas power, respectively). It should be noticed that layers formed in conditions of higher r.f. power contain also the nitride phase, as evaluated by means of ellipsometry. For longer (10 min) oxidation times the tendency is similar, although the layer thickness for higher power is exceptionally high.
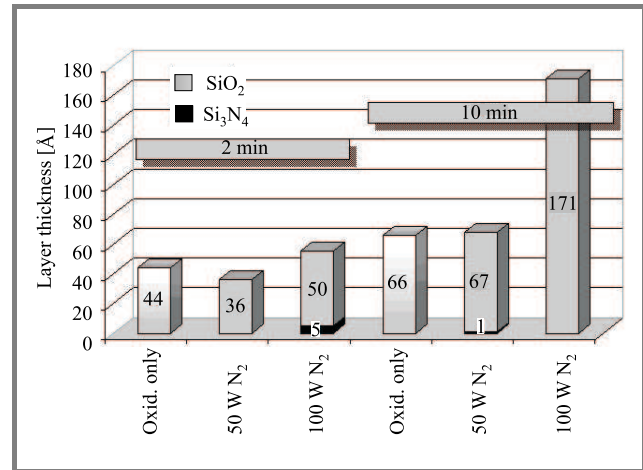

Fig. 3. The total and component-layer thickness (as evaluated using the EMA model) of the layers obtained by plasma oxidation of samples exposed to nitrogen plasma. The results of plasma oxidation only are used as a reference.

When analysing the possible reasons for such results we have to take a complex nature of the processes into consideration. One should be aware of the fact that apart from the amorphisation (damage) of the silicon subsurface region, the creation of SiN bonds (even at $350°C$) is also possible in nitrogen containing plasma. The latter effect is possible due to the damage (broken bonds) resulting form nitrogen ion bombardment.

Thus, we have to consider two contradictory effects during plasma oxidation (stage 2). While oxide growth is slowed down by the presence of SiN bonds, at the same time it is also accelerated by the presence of broken silicon bonds in the subsurface region. Additionally, we have to remember that nitrogen atoms tend to be replaced by oxygen atoms in position bonded to silicon during oxidation even at such low temperatures.

The use of ammonia plasma results in a different behaviour from that observed in nitrogen plasma (compare Figs. 3 and 4). In all experiments of this series the final oxynitride layer thickness is lower than that obtained during reference oxidation, which proves the effective passivation of silicon surface by nitrogen implantation from ammonia. It is interesting to note that the nitride-phase content is much higher in these samples than in all those described before. Moreover, in contrast to previous cases, the oxidation time does not have much influence on the layer thickness. A careful look at Fig. 4 indicates that the dependencies of layer thickness on r.f. power are different for shorter and

longer oxidation times in this case. This obviously confirms the hypothesis presented above of different effects competing with one other during the stage 1 and stage 2 processes.
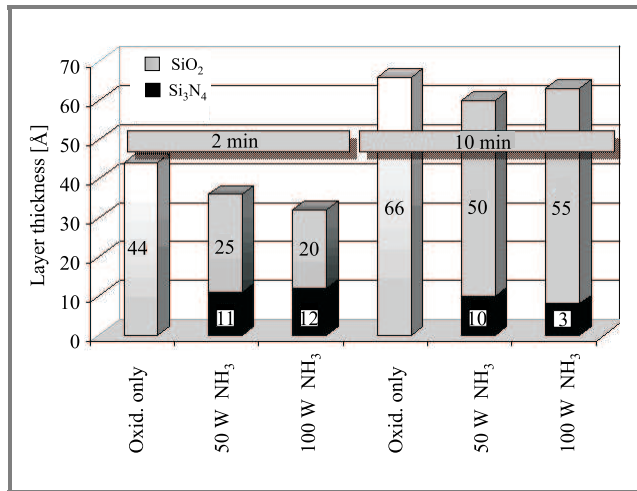

Fig. 4. The total and component-layer thickness (as evaluated using the EMA model) of the layers obtained by plasma oxidation of samples exposed to ammonia plasma. The results of plasma oxidation only are used as a reference.

Taking into consideration that both effects are caused by the phenomena taking place only in the ultra-shallow, subsurface region, we have to remember also that all these effects will disappear if an oxide layer thick enough is grown (thick enough to consume the affected silicon depth).

As a consequence, oxidation slow-down takes over for short oxidation times the, while oxidation rate is enhanced by broken silicon bonds for long enough oxidation times (longer than it takes for all or most of the nitrogen to be removed from the layer). This enhancement will continue until the whole silicon region affected by ion bombardment is consumed by the growing oxide.

Even during oxidation, at such low temperatures (350°C) the nitrogen atoms incorporated and bonded with silicon during the earlier process (stage 1) tend to be replaced by oxygen. As a result, the nitrogen content in the oxynitride layer is dependent on the oxidation time and inevitably tends to decrease during oxidation. The latter effect is very effective, as can be seen using the 100 W N$_2$ plasma process as an example. As the result of oxidation results in a ~170 Å oxide layer with no nitride phase present, as evaluated by spectroscopic ellipsometry (see Fig. 3).

The situation is little different, when ammonia plasma is used instead of nitrogen. As can be seen in Fig. 3, the nitride-phase content is much higher then, when compared with nitridation carried out in N$_2$ plasma. This observation can be explained by a well known fact that ammonia dissociates much easier in plasma than nitrogen. Consequently, for both short (2 min) and longer (10 min) oxidation times we can still observe the nitride phase in the layer.

It is also interesting to note that in the oxynitride layers formed by the oxidation silicon exposed previously to NH$_3$ plasma the nitride content does not change much between 2 min and 10 min oxidation times (compare Fig. 4). It seems that nitrogen replacement with oxygen is not so effective during oxidation in this case. The most probable hypothesis explaining this effect refers again to more effective formation of nitrogen in NH$_3$ plasma, which in turn allows thicker and denser nitride phase to be formed during this stage of experiment. Denser and more perfect nitride component may be less prone to oxygen replacement during plasma oxidation at low temperatures (< 350°C).

As it was already mentioned above, the oxidation rate is influenced by all the effects described above until the whole affected silicon subsurface region becomes oxidised. It is, therefore, crucial for understanding of the whole process to be aware of the range of the distances covered in the silicon substrate by ions implanted from r.f. plasma. As already mentioned before, this information may only be obtained by means of appropriate simulations or experimental measurements of the implantation depth (profile) and doses.

The energies of ions bombarding silicon samples in a PECVD planar reactor are expected to be very low – depending on the pressure and r.f. power used they could amount to a few hundreds of volts or even less. The only simulator that allows such low ion energies to be considered is TRIM [5] (a part of SRIM simulator). The problem in this case is, however, that no data is available on the accuracy of this simulator for such an energy range.

On the other hand, due to the fact that the expected penetration is within the ultra-shallow range, the measurements require extremely high in-depth resolution which, until recently, could not be reached. Only recently, the progress made in medium energy ion spectroscopy (MEIS) allowed some unique experimental data to be obtained.

In [6], the results of MEIS measurements of nitrogen profile implanted into silicon at very low energies (200 eV, 500 eV and 1000 eV) may be found. This gave us a unique chance to compare the MEIS profiles with those obtained by means of TRIM simulations assuming the same ion energies. The results of theoretical calculations by TRIM for all three energy values (i.e., 200 eV, 500 eV and 1000 eV) are compared with the MEIS profiles in Fig. 5.

Looking carefully at this figure one may notice obvious differences between the calculated and measured ion profiles. The TRIM profiles are certainly deeper than those obtained by MEIS. The relative differences between the individual ion ranges obtained by both methods are, however, very similar.

The simulated and experimental profiles differ also by the total number of nitrogen ions located within the silicon substrate per implanted ion. The lower total densities of implanted ions received for MEIS profiles seem to prove that more ions than expected by TRIM simulations are un-

able to penetrate the silicon substrate. This can possibly be explained by more effective backscattering from the silicon surface than calculated by TRIM.
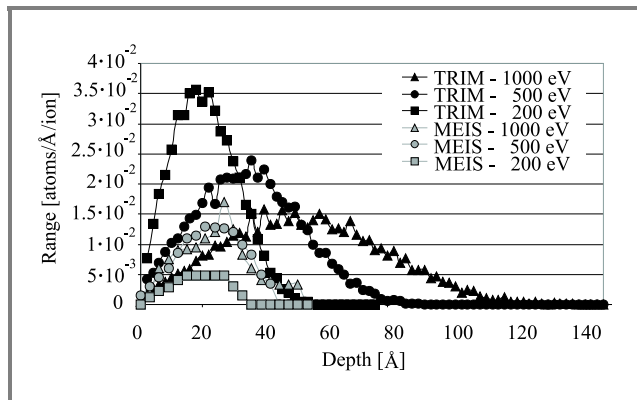

Fig. 5. Comparison of the nitrogen profiles in silicon determined experimentally by means of MEIS [6] and the results of TRIM simulation assuming the same energies of nitrogen ions (i.e., 200 eV, 500 eV and 1000 eV).

Despite the observed differences, it should be noted that in both cases the implanted nitrogen profile depths are of the same range (or higher) than the thickness of oxyntiride layers for state-of-the-art MOSFET gate stacks. This means, that ultra-shallow implantation of nitrogen from r.f. plasma will always play a very important role in the formation of ultra-thin oxynitride layers, especially when low thermal budget is at stake.

4. Conclusions

Within the scope of this work it has been proved that the process of nitrogen implantation takes place even in PECVD r.f. plasma. It influences the kinetics of oxynitride layer growth and the properties of the resulting layers. This ultra-shallow implantation affects the final oxide (oxynitride) layer thickness and its composition by three mechanisms. These are: damage of the substrate during ion implantation from r.f. plasma, formation of SiN bonds (in the case of nitrogen containing plasmas), and replacing the nitrogen in SiN bonds by oxygen during oxidation (even at low temperatures – 350°C). It should be also noted that all of these processes take place "dynamically" while consuming the substrate during oxidation.

The results of nintrogen implantation from nitrogen and ammonia plasmas are different. In the former case even short low-temperature oxidation results in the formation of almost pure oxide – the nitride phase is hardly seen there. The case is different for ammonia plasmas. We obtain true oxynitride layers, as the nitride-phase content may even amount to 30% for short oxidation times.

The depth range of the nitrogen implantation under low-energy conditions has been evaluated by means of TRIM simulations and compared to MEIS measurements found in [6]. Although the TRIM profiles exhibit deeper penetration range than that obtained by MEIS and TRIM seems to underestimate the backscattering from the silicon surface, in both cases the nitrogen implantation depth is higher than the thickness of oxynitride layers required in state-of-the-art CMOS ICs.

Acknowledgements

References

[1] ITRS – International Technology Roadmap for Semiconductors, http://www.public.itrs.net

[2] J.-P. Carrere, A. Grouillet, F. Guyader, A. Beverina, M. Bidaud, and A. Halimaoui, "Triple gate oxide by nitrogen implantation integrated in a 0.13 μm CMOS flow", in *Proc. 32nd Eur. Solid-State Dev. Res. Conf. ESSDERC 2002*, Bologna, Italy, 2002, pp. 155–158.

[3] C.-C. Chen, M.-C. Yu , J.-Y. Cheng , M.-F. Wang , T.-L. Lee, S.-C. Chen, C.-H. Yu, M.-S. Liang, C.-H. Chen, C.-W. Yang, and Y.-K. Fang, "Characterization of plasma damage in plasma nitrided gate dielectrics for advanced CMOS dual gate oxide process", in *7th Int. Symp. Plas. Proc. Induc. Dam.*, Santa Clara, USA, 2002; *Amer. Vac. Soc.*, pp. 41–44, 2002.

[4] R. B. Beck, T. Bieniek, A. Wojtkiewicz, and A. Jakubowski, "Low temperature plasma oxidation of silicon – possibility of application in CMOS-ULSI technology", in "Advances in Plasma Chemistry" *Acta Agrophys.*, vol. 80, pp. 247–256, 2002.

[5] J. F. Ziegler, http://www.srim.org

[6] E. P. Gusev, H. C. Lu, T. Gustafsson, E. Garunkel, M. L. Green, and D. Brasen, "The composition of ultra-thin oxynitrides thremally grown in NO", *J. Appl. Phys.*, vol. 82, p. 896, 1997.
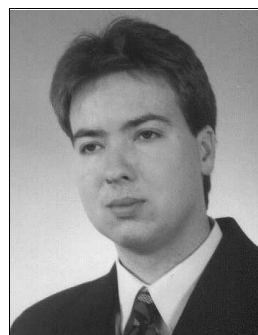
Tomasz Bieniek was born in Warsaw, Poland, in 1977. He received the M.Sc. degree from Warsaw University of Technology in 2002. He is currently working towards a Ph.D. degree. His research area concentrates on plasma processes for CMOS-VLSI technology.

e-mail: tbieniek@elka.pw.edu.pl
Institute of Microelectronics and Optoelectronics
Warsaw University of Technology
Koszykowa st 75
00-662 Warsaw, Poland

Romuald B. Beck graduated from the Faculty of Electronics, Warsaw University of Technology, in 1977 and joined the Institute of Microelectronics and Optoelectronics the same year. He received the Ph.D. and D.Sc. degrees in 1985 and 1996, respectively. His research activities are concentrated in the area of modeling, diagnostics and technology of metal-insulator-semiconductor structures, especially with very thin and ultra thin oxide. His work is focused on theoretical and experimental studies of different methods of dielectric-layer formation (including those involving DC and AC plasma) and their kinetics, as well as the yield, electrophysical properties and reliability of the resulting devices. His research interests include also dry etching methods and their implementation in modern IC and MEMS technology. He authored and co-authored more than 90 technical publications.
e-mail: beck@imio.pw.edu.pl
Institute of Microelectronics and Optoelectronics
Warsaw University of Technology
Koszykowa st 75
00-662 Warsaw, Poland

Andrzej Jakubowski received the M.Sc., Ph.D. and D.Sc. degrees from the Faculty of Electronics, Warsaw University of Technology. At present he is the Head of the Division of Microelectronics and Optoelectronics Devices in the Institute of Microelectronics and Optoelectronics (WUT). In the years 1989–1992 he held the position of the Director of the Institute of Electron Technology in Warsaw. From 1989 to 1991 he was the head of the Government Program for Polish Microelectronics. In the years 1990–1991 he headed Polish Government Committee on Applied Sciences. The main area of his research interests is modeling, characterization and technology of semiconductor structures and integrated circuits. He is also the author and co-author of approximately 400 technical papers.
e-mail: jakubowski@imio.pw.edu.pl
Institute of Microelectronics and Optoelectronics
Warsaw University of Technology
Koszykowa st 75
00-662 Warsaw, Poland

Andrzej Kudła – for biography, see this issue, p. 39.