

ANODIC DISSOLUTION OF SILICON BY ELECTROCHEMICAL CARRIER CONCENTRATION PROFILING

Rudolf Kinder — Juraj Breza — Fedor Mika — Alena Grmanová *

Anodic dissolution of an epitaxial layer and of a boron implanted epitaxial layer in a solution of ammonium bifluoride ($\text{NH}_4\text{F}.\text{HF}$) has been studied. An optimized set of parameters for carrier concentration $N(x)$ profiling has led to a choice of the bias voltage and determination of the effective valence number of $z = 3.3$ for the boron implanted epitaxial layer and $z = 3.5$ for the unimplanted epitaxial layer.

Keywords: ECV technique, current voltage curve, carrier concentration profile, silicon, valence

1 INTRODUCTION

The electrochemical capacitance-voltage (ECV) technique is used for carrier concentration profiling $N(x)$ of semiconductors layers. In the ECV technique, a semiconductor sample creates a Schottky contact with the electrolyte solution. At the same time, the electrolyte is chosen in such a way that it gradually etches the selected area thus allowing measurement of the $N(x)$ profile over any arbitrary thickness. Unlike in the case of III-V semiconductors InP and GaAs, silicon forms a non-soluble oxide SiO_x ($x = 1.7 - 1.9$) at the surface during anodic oxidation. By a purely chemical reaction, fluoride ions (ammonium bifluoride) dissolve this oxide in the electrolyte. Even though the rate of formation of the oxide is proportional to the current density, the rate of its dissolution depends basically on the composition of the electrolyte and on the properties of silicon.

The properties and characteristics of the silicon-electrolyte interface have been extensively investigated in the past years. This interface is interesting from several points of view. One of them is the formation of silicon-on-insulator structures by oxidation of buried porous silicon layers [1]. The problems are mainly manifested in the uncertainty of the effective dissolution valence number z (the number of electronic charges transferred per atom of silicon dissolved) and consequently in the reduced accuracy of depth calibration. It has been long recognized that a number of reactions can be involved in the electrochemical dissolution of silicon. The effective dissolution valence number may vary within the range from 2 to 4 [2]. The first attempts to measure the $N(x)$ profile by ECV of silicon [3] showed that even at carefully chosen working conditions the valence number varied in the range 3.3 -

3.8 depending on the electrolyte, on the quality of the silicon sample and on other factors.

According to work [3], for p-type silicon is $z = 3.72$ at an anodic dissolution process in a 0.1 M solution of $\text{NH}_4\text{F}.\text{HF}$, while for implantation layers in epitaxial substrate is $z = 3.3$, [4].

Extraction of z parameter for the $N(x)$ profile by ECV measurement can be achieved in two ways. One of them is to obtain the value of z parameter experimentally. The value of z is optimal when the depths of $N(x)$ profiles obtained by ECV technique and Talystep profiler are comparable. The second means can be the procedure presented in [1]. The $N(x)$ profile is measured on a set of reference samples to a few different depths. Faraday's law is used in the ECV method to calculate the etch depth, x_r , by integrating the etch current I :

$$x_r = \frac{M}{Fz_r D A} \int Idt. \quad (1)$$

Here, F is the Faraday constant, z_r is a predefined value for the effective valence number, A is the dissolution area, M and D are the molecular weight and density, respectively. Then, the final crater depth x_m is measured by Talystep, which is related to the actual valence number z according to

$$x_m = \frac{M}{Fz D A} \int Idt. \quad (2)$$

After substitution of (1) into (2) we have

$$x_m = \left(\frac{z_r}{z} \right) x_r. \quad (3)$$

The actual z parameter can be obtained by linear regression of the dependences $x_m = f(x_r)$ and from

* Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Microelectronics, Ilkovičova 3, 812 19 Bratislava, Slovakia

expression (3) or from the slope of the curve. This value of z can be used to measure the $N(x)$ profile of the semiconductor sample.

In this paper, attention is focused on the properties of the electrolyte-silicon interface and on its influence upon the carrier concentration profile $N(x)$. The anodic dissolution process of p-type silicon in the solution of $\text{NH}_4\text{F}\cdot\text{HF}$ is examined from the point of view of the etching voltage and z parameter. Optimized parameters for defined etching of the $N(x)$ profile by ECV technique could be given. The $N(x)$ profiles obtained with ECV technique are compared with profiles measured by the spreading resistance (SR) method and the epitaxial layer is compared with the doping profile calculated by SUPREM.

2 EXPERIMENTAL RESULTS

ECV analysis was carried out with profiler Polaron PN4100. The ECV measurements were obtained using carrier and modulation frequencies of 3 kHz and 30 Hz. The parameters for $N(x)$ profile measurements are determined by measuring the current-voltage ($I - V$) and conductance and capacitance-voltage ($G/C - V$) curves. These curves contain information about the voltages for etching V_{etch} and measuring V_{meas} .

Experimental measurements with ECV equipment were conducted on a boron implanted epitaxial layer (hereafter implanted sample) and on an unimplanted epitaxial layer. The first sample was p-type Si (100), substrate concentration $2 \times 10^{18} \text{ cm}^{-3}$ with an epitaxial layer (concentration $5 \times 10^{14} \text{ cm}^{-3}$, time 15 minutes, 1050°C). The sample was boron implanted through an SiO_2 layer (thickness 100 nm) with an energy of 100 keV and dose of $1.5 \times 10^{13} \text{ cm}^{-2}$. The sample was activated in dry O_2 ambient at a temperature of 1100°C for 100 minutes. The second sample was p-type Si (100), (substrate concentration $3.2 \times 10^{18} \text{ cm}^{-3}$, with a $\approx 11\mu\text{m}$ epitaxial layer, boron doped to $4 \times 10^{14} \text{ cm}^{-3}$, time of epitaxial growth 12 minutes, 1176°C).

The electrolyte used was a 0.1 M solution of $\text{NH}_4\text{F}\cdot\text{HF}$ with one drop per 100 ml of Triton X 100 acting as a non-ionic wetting agent. Before inserting the samples into the electrochemical cell, the samples were shortly dipped in concentrated HF (8%) to etch the thin oxide layer, then rinsed several times in distilled water and dried. Good ohmic electrical contacts were made by scratching the surface (on the back side) whilst applying eutectic (Ga-In). Before being filled, the electrochemical cell had to be cleaned using distilled water and dried carefully to ensure a defined electrolyte concentration. The best result was obtained by cleaning the tested area using a blower through the hole of a pump chamber of the cell body just after filling the cell with $\approx 2 \text{ ml}$ of electrolyte and then filling the cell up with electrolyte. The anodic process is accompanied with the creation of a gaseous product. To remove the gaseous product from the silicon surface generated by the anodic dissolution process, the

ECV equipment incorporates a pumping system. For the ECV measurements of silicon to be successful, anodic dissolution should be reproducible and uniform and the electrolyte-semiconductor interface should approximate a Schottky contact. Anodic dissolution behaviour depends mainly on the stripping voltage (V_{etch}), illumination level (for n-type Si) and parameter z .

The first information on the electrochemical dissolution process can be deduced from $I - V$ characteristics taken in the anodic voltage regime. Figure 1 shows a typical $I - V$ curve measured on the first sample, for determining the value of V_{etch} .

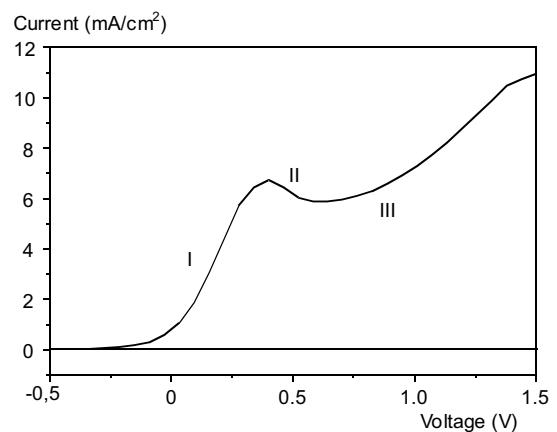


Fig. 1. Typical $I - V$ curve of an implanted sample

In Fig. 1 it can be seen that the anodic behaviour of silicon is strongly dependent on the applied voltage. First the initial voltage is increased linearly (exponential region - I) because of formation of an isolating oxide, then the current decreases (transition -region II). Subsequently it begins to increase again (electropolishing region - III). From these electrochemical results it was obvious that smooth and homogeneous etching of silicon could be carried out only at potentials corresponding to the electropolishing region where the dissolution of silicon occurs through the dissolution of an oxide film which is readily formed on the electrode surface.

Another important parameter is the valence number. The values of z for samples with implanted and epitaxial layers were determined experimentally. For epitaxial and implantation layers of samples we obtained $z = 3.5$ and $z = 3.3$, respectively. The same results were obtained with the procedure mentioned above. Here, the predefined value for the effective valence number was $z_r = 3.8$. Using this value of z_r , the $N(x)$ profiles were measured to a few different depths. Using the depths measured by Talystep (x_m) and by ECV (x_r), we have plotted the x_m versus x_r dependences. The actual value of parameter z was obtained by linear regression of the $x_m = f(x_r)$ dependence. The z parameter for homogeneous and implanted silicon samples was calculated from expression

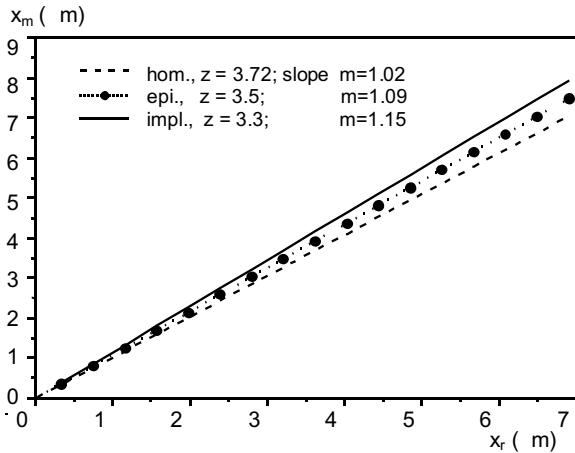


Fig. 2. Dependence x_m versus x_r allowing to extract the z parameter for homogeneous, implanted and epitaxial layers in silicon.

(3). Dependences $x_m = f(x_r)$ for three samples are seen in Fig. 2.

The linear curve with a slope of $m = 1.02$ (for $z = 3.7$) was obtained for a homogeneous Si sample. The other curves belong to the unimplanted epitaxial sample ($m = 1.09$; $z = 3.5$) and implanted sample ($m = 1.15$; $z = 3.3$). The dependence $x_m = f(x_r)$ was obtained for etched depths up to $7\mu\text{m}$. From the dependence it is seen that z does not depend on the etched depth.

The accuracy of determining the z parameter can be seen from a comparison of $N(x)$ profiles measured by ECV and SR method or calculated with SUPREM.

Figure 3 shows the $N(x)$ profiles of the boron implanted epitaxial layer measured by ECV technique at $V_{meas} = -0.3$ V and $V_{etch} = 1.4$ V, at $z = 3.3$, and measured by SR method. In practice it can be assumed that z has an average value because the rate of etching of the implanted layer is larger than that of the epitaxial layer.

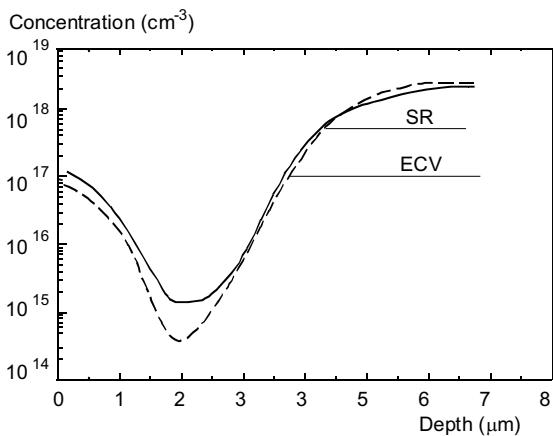


Fig. 3. Concentration profile $N(x)$ of a sample implanted by boron through an SiO_2 layer into the epitaxial layer as determined by SR and ECV techniques.

From Fig. 3 it can be seen that a discrepancy is typically observed in the absolute doping levels measured with various techniques. In the case of heavily doped p -type silicon, the ECV result for carrier concentration is slightly lower than that obtained from SR measurement. This is in contrast to the situation at low doping levels, where the ECV result was substantially higher. This may be caused by various factors such as the contribution of deep states to the $C-V$ curve or imperfect calibration of the SR method. The concentration on the sample surface, in comparison with SR, is better determined by the ECV technique. The surface morphology of the etched sample was checked by Talystep measurements. The crater bottom was smooth and etched into a depth of $7.1\mu\text{m}$, which is about $0.1\mu\text{m}$ less than in ECV measurements. The good agreement of the depth profiles $N(x)$ obtained by SR and ECV profiling indicates that the determination of the parameter z for electrochemical dissolution was performed quite correctly.

The $N(x)$ profile of the sample with an epitaxial layer was measured at $V_{meas} = -1$ V and $V_{etch} = 1$ V, at $z = 3.5$. The profile measured by the ECV technique is seen in Fig. 4.

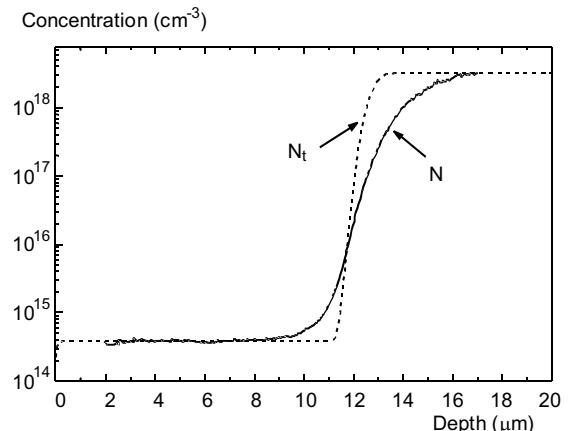


Fig. 4. The $N(x)$ profile of the epitaxial layer in silicon as determined by ECV techniques and calculated by SUPREM.

From Fig. 4 it is seen that the $N(x)$ profile of the epitaxial layer (measured at $z = 3.5$) in comparison with the doping profile $N_t(x)$ calculated by SUPREM is influenced by autodoping. The difference between the carrier density and the impurity distribution can be significant in the region of the abrupt change in the doping distribution. We have found from Talystep measurements that the bottom of the etched craters was flat and the depth of the crater was $17.5\mu\text{m}$. The measured depth of $N(x)$ profile by ECV technique was $\approx 18\mu\text{m}$ (Fig. 4). Good agreement of the measured depths (by Talystep and ECV) is clearly seen.

3 CONCLUSION

The analysis of the anodic dissolution behaviour of p-type of silicon solution of NH₄F.HF has been investigated. The manner of calculating the average value of the valence number at profiling semiconductors layers in silicon is reported. It is found that the value of the valence number depends on the kind of measured layers (implanted, epitaxial, etc.). It follows from the results mentioned above that in the case of accurate profiling of structures containing silicon layers with different electrical behaviour (parameter z), the electrochemical dissolution process must be investigated for each layer separately.

Acknowledgements

This work was supported by the Ministry of Education of the Slovak Republic (Grants No. 1/7613/20).

REFERENCES

- [1] PEINER, E.—SCHLACHTZKI, A.: J. Electrochem. Soc. **139**, No. 2 (1992), 552 - 557.
- [2] ARITA, I.: Crystal Growth **45** (1978), 383 - 392.
- [3] SCHARPE, I. C. D.—LILLEY, P.: Electr. Letters **15** No. 20 (1979), 622 - 624.
- [4] KINDER, R.: Phys. stat. sol. (a) **164** (1997), 785 - 789.

Received 14 May 2001

Rudolf Kinder (Doc, Ing, PhD) was born in Pezinok in 1940. In the sixties, he worked in electrotechnical industry in Bratislava. Then he worked at VURUP (Research Center

for Petrol Chemistry) in the field of automation of chemical services. He graduated in technical cybernetics from the Faculty of Electrical Engineering, Slovak Technical University, Bratislava. He received a PhD degree in electronics and vacuum technology in 1984. He has worked as a senior scientist since 1989. Since 1996 he has been associate professor in microelectronics. His research activities are oriented towards semiconductor technology, particularly to analysis and simulation.

Juraj Breza (Doc, Ing, PhD) born in Bratislava in 1951, graduated in solid state physics in 1974 and received his PhD degree in electronics and vacuum technology in 1982, both from the Slovak Technical University. Since 1985 he has been associate professor in microelectronics. His teaching and scientific activities include materials analysis, thin films and surface science.

Fedor Mika (Ing, PhD) was born in Bratislava in 1949. He graduated in microelectronics from the Faculty of Electrical Engineering of the Slovak Technical University (STU), Bratislava, Slovakia. He received the PhD degree in microelectronics from STU in 1989. Since 1972 he has been with Microelectronics Department of STU as an Assistant Professor. His research interests are in the areas of solid states structures, devices and electronic instruments. He can design and realize special measurement units in the area of parameters measuring of solid state structures and devices and in the measurement of the noise properties of electronic devices.

Alena Grmanová (RNDr) comes from Nitra, Slovakia. She received her doctorate in chemistry from Comenius University in Bratislava. Having spent some time in industry, at present Alenka is engaged research at the Slovak Technical University. Her scientific interests include chemical processing of semiconductor materials, thin films and surfaces.

Brno 25-26 September 2002



Department of Electrical Engineering and Electronics
of Military Academy in Brno
Institute of Electromagnetic Theory
of Faculty of Electrical Engineering and Communications
of Technical University in Brno

Seminar on Theory of Electric Circuits

New Trends in Teaching Electrical Engineering and Electronics
organized under auspices of deans of the faculties of
Avionics and Anti-aircraft Forces of Military Academy in Brno and
Electrical Engineering and Communications of Technical University in Brno

The aim of seminar is to exchange the computer aided teaching and research experience in electrical engineering. Oral and poster presentations are considered and exhibition of teaching aids, equipment and programme systems will be held by involved departments and the sponsoring companies.

The seminar is open for contributions namely from the teaching of electrical engineering and electronics subjects:

- Methodology of teaching more complicated parts of the system theory, circuits and signals
- New methods of signal processing: neuron networks, adaptive and nonlinear filtration
- Programmes and technological means for digital signal processing
- Utilization of computation techniques in practical and laboratory exercises
- New algorithms in circuit theory
- New trends in design and fabrication of circuits
- CAD/CAM in teaching of electrical engineering subjects
- Modern streams in analysis and synthesis of electric circuits
- System treatment in circuit theory teaching
- Electromagnetic theory issues

Deadlines:

Papers submission: 15. May 2002, Acceptance acknowledgement: 10. June 2002, Registrations and payment: 1. July 2002.