Model of nanodegradation processes in electronic equipment of NPP Kozloduy

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Abstract. From the complex studies it was proof that the main degradation processes in the three groups of elements for the extended period of time are slow; do not lead to a hopping change in basic parameters and to catastrophic failures. This gives grounds to suggest a common diffusion model, which is limited to the following: -in electronic components containing a p-n junction, is performed diffusion of residual cooper atoms, that are accumulated in the area of a spatial charge under the influence of the electric field and the local temperature, creating micro-shunt regions; -in the contactor systems whose contact surfaces are made of metal alloys under the influence of increased temperature starts decomposition of a homogeneous alloy. Conditions are created for diffusion of individual atoms to the surface, micro-phases of homogeneous atoms are formed and modify the contact resistances; -in the course of time in the insulating materials are changed the mechanisms of polarization, double bonds and dipoles are disrupting, leading to the release of carbon atoms. The latter diffuse at elevated temperatures and form conductive cords, which amend the dielectric losses and the specific resistance of the materials.

1. Introduction
A general physic model for slow degradation of electronic systems equipment with continuing resource is developed on the base of analyses of elemental diffusion processes in three separate groups of the component base: semiconductor diodes and transistors; electric contactor systems; dielectric materials.

Physical models of degradation processes in the three types of specimen are based on diffusion processes that allow accepting a general driving mechanism – diffusion of material particles, independently of their origin. There are accepted as general parameters of degradation the following factors:

- coefficient of ideality factor $\beta$ for selected diodes and coefficient of conductivity $h_{21}$ for selected transistors;
- microhardness $H$ and contact resistance $R_k$ for selected mechanical contactors;
- dielectric losses $\tan \delta$, dielectric permittivity $\varepsilon$ and high voltage voltampere features are selected insulation materials.

2. Semiconductor diodes and transistors
Measurement of electrical parameters of semiconductor specimens is performed and analyzed by theoretical model proposed by A Popov [1] and used into methodology developed from us [2-4]. It is based on shunt areas in p-n junction of diodes and transistors in continuous operation which change their voltampere characteristics and respectively the rest of the current parameters. Diffusion and accumulation of residual impurity atoms with small covalent radius in dislocation defects that occur in
process of technological formation of active semiconductor structure are shown in cases (a, b, c in figure 1). They are considered as main reasons for formation of real shunting areas (case a). Another cases (b,c) form single deep levels and clusters. Formation of shunt areas and clusters that create deep levels into the forbidden zone influences most strongly on voltampere characteristic of p-n junction and in particular of the coefficient $\beta$ (ideality coefficient) into the formula:

$$I = I_o \exp\left(\frac{qU}{\beta kT}\right)$$

The change of ideality coefficient shows that the tilt of volt-ampere characteristics of the p-n junction alters and respectively the current parameters of the simple diode created on the base of it are changed.

In regard to bipolar transistor created on the base of two p-n junctions (emitter and collector transitions) the current of collector transition $I_{ko}$ changes mostly, the ratio of electricity transition by current $h_{21}$ as well as and the slope of voltampere family features.

The explanation of this degradation phenomenon can be traced to the model based on the modification of the spatial charge of the p-n junction because the formation of shunt areas after accumulation of impurity atoms on the dislocation defects. The spatial charge is presented in figure 2 in a three-dimensional version with shunt field. Ideality coefficient of this p-n junction is presented with this expression [8,9]:

$$\beta = \left\{ \frac{2}{b+c} \right\} (\omega / L)$$

where $\omega = x_n + x_p$ is the width of the spatial charge, $L$ - diffusion length of the carriers and $b$ is the ratio between the mobility of electrons and holes.

Shunt areas formation and deep levels in sensitive concentrations, influencing on current parameters of diode and of transistor increase the value of the ideality factor as is shown in figure 3. In this case the relation between the width of the spatial charge and diffusion length of carriers increase (become bigger than zero) because of the spatial charge length increasing. The changes of a static current transfer constant $h_{21}$ of a non-operated (upper curve) and 10-year operated (lower curve) transistor KT310 2B are presented in figure 4. About aging process it is proposed following mechanism:

- diffusion of impurities with a small covalent radius into dislocations intersecting p-n junction, and forming a shunt fields with a high conductivity;
- as main diffusing element are considered copper atoms contained in the synthetic semiconductor crystals in high enough concentrations, and are with significantly smaller covalent radius than that of the main atoms of the basic crystal;
effective coefficient of copper atoms diffusion is defined assuming that the quantity of accumulated impurities is proportionally to the operational time and temperature of p-n junction. Radius of the dislocation tube is assumed to be equal to the lattice parameter of < 10 Å. The copper diffuses into silicon as positively charged ion. The coefficient of diffusion into n-type and proper silicon is [5]:

$$D_{\text{int}} = (3.0 \pm 0.3) \times 10^{-4} \exp \left( \frac{-0.18 \mp 0.01 \text{eV}}{k_B T} \right) \text{ cm}^2 \text{s}^{-1} \quad (3)$$

Positively charged copper ion form couples with negatively charged acceptor ion- boron and consequently a portion of the dissolved copper ions are stationary. The effective diffusion coefficient of copper in the silicon alloyed with boron, [6] is:

$$D_{\text{eff}} = 3 \times 10^{-4} \exp \left( \frac{-2090/T}{1 + 2.584 \times 10^{-20} \exp(4990/T)(N_a/T)} \right) \text{ cm}^2 \text{s}^{-1} \quad (4)$$

In p-type silicon the copper forms copper-copper pairs. The analysis shows that they are formed
between atom in node and atom in internode. The time of the dissociation of the copper-copper couples is [7]:

$$\tau_{\text{Cu-pair}} = 1.47 \times 10^{-10} \exp \left( \frac{1.02 \pm 0.07 \text{ eV}}{k_B T} \right) \text{ s}$$ (5)

This equation gives time constant from 16 days to 9.5 years. The average value is about 8 month. Process with such a constant can be completely decisive for the slow degradation of silicon diodes and transistors. The lifetime in n-and p-silicon vary in a different manner depending on copper concentration. Influence of lifetimes and its changes on voltampere characteristics of p-n junctions is well described from the model of Stafeev [8, 9].

Take the real values for lifetimes of electrons and p-carriers, measured into alloyed with copper n-Si and p-Si, are obtained $\beta \approx 2$ at low alloying. At higher level of alloying where lifetimes are obtained, is measured $\beta \approx 3$. By this model smooth growing of $E$ could be explained with lifetimes amendment at low alloying. The large changes of $\beta$ (3-7) are due to amendments of times at very high alloying with copper. From the analysis of the above models, combined with the experimentally obtained data it is built a theoretical model for the slow degradation of diodes and transistors, which are a major elemental base in electron equipment for the management and control of NPP. For diodes the analytical form of the model is represented by equation (6) and graphically presentation in figure 5:

$$\beta = (0.066 \pm 0.042) \times \text{Years} + (1.49 \pm 0.238)$$ (6)

For transistors the analytical form of the model is represented by equation (7) and graphical presentation in figure 6:

$$h_{21} = (-8.006 \pm 5.033) \times \text{Years} + (162.758 \pm 28.473)$$ (7)

Figure 7 shows that the relative increase of the ideality factor $\beta$ of tested diodes is in the range 1.15 – 1.8. A similar picture was seen in the relative change of the transmission of the tested specimens. On the basis of the known values of the coefficient of diffusion of cooper into silicon and the dynamics of the
Figure 6. Graphical presentation of transistors aging as a function of the operating time ($Y = h_{21}, x = \text{years}$).

Figure 7. Relative increase of $\beta$ of the tested diodes.

Figure 8. Arbitrary changes of $h_{21}$ tested transistors.

formation and destruction of couples of cooper ions and precipitates were evaluated time constants of the degradation processes of about 15 days to more than 9 years.

2. Electro-contact systems
The second main group of elementary base of electronic equipment of NPP were electro contact systems, for which are studied: i) ampere-volt features of couple of pairs of contacts from each contactor for determine of contactor resistance $R_{k}$; ii) micro-hardness $H$ of constant surfaces of unused and used contactors independently of light and dark areas where they are detached; iii) ampere-volt characteristics for defining of surface-resistance $R_{s}$, separately of light and dark regions of contact areas (of unused and used contactors).

2.1 Measurement and analysis of contact resistance of contacts in mechanical contactor systems
The first and most important performance parameter for all contactor devices with mechanical metal contacts (or metallurgical contacts, such as thermocouples and some other control devices) is their contact resistance $R_{c}$. It is extremely sensitive to any degradation processes and its quantitative values
are an indicator of whether the contactors have entered a phase of ageing or are in conditions of normal operation. Characteristic for the beginning of this degradation process is the relative increase of the contact resistance between the contacting pads, measured in closed contact. For its determination a method of comparative measurement of the residual potential difference between the contact spots in operating position of the used and unused contactors of the same type is used. Measurement is done by a four electrode method – a modified two probe method (Figure 9a). According to the equivalent scheme as shown (Figure 9b) the residual potential difference $U_{12}$, registered by the voltmeter is determined by the contact resistance between the contacting pads.

$$R_k = R_{k1} + R_{k2} = \frac{U_{12}}{I}$$

(8)

The potential probes are located in close proximity to the contact spots, so that the measured potential difference $U_{12}$ reads the voltage drop mainly on a high resistive component of the near contact layers, designated with $R_k$. Reference measurements of used and unused contactors of the same type replace the absolute geometric calibration. This paragraph describes measurements done to study the contact resistance of mechanical contactors. Described measurements are non-destructive and are carried out under normal pressure on contacts: of an activated contactor for normally open contacts and of non-activated contactor for normally closed contacts and in currents comparable to the nominal ones for operation. After summarizing the results, on selected representative contact couples are modeled volt-ampere features. Furthermore, again on the selected contacts are made electric probe measurements, as well as, a study of micro-hardness and position by an X-ray microprobe. Potential probes are placed as close as possible to the contact spots, so that the measured potential difference $U_{12}$ reads the voltage drop mainly on the high resistive component of the near contact layers, designated with $R_k$.

2.2 Measurements of micro-hardness

The study of micro-hardness contactor spots are performed using micro-hardnessmeter. Measurements are conducted at room temperature. The pressure on the intender $P$, could be selected in the interval 0.5-200g. By software is calculated the average micro-hardness for a given loading:

$$H = \frac{AP}{d^2},$$

(9)

where the value of the constant $A$ depends from the type of the selected indenter. At the same time are calculated the deviations from the average value of $H$, as well as the depth of indenter penetration into the specimen, $d$. In order to examine the profile of change in the micro-hardness as a function of the penetration depth of indenter, measurements are carried out over a wide range of load - by at least such that it is possible to measure the fingerprint, to one in which to reach a steady characteristic for a given material micro-hardness. A comparison of the profiles of unused and used specimens can show whether there have been changes in the mechanical properties of the surface layer under the influence of the operating conditions (corrosive atmosphere, high temperature, humidity, radiation). The method may also be used in carrying out the phase analysis. If the specimen is multiphase and different phases are large enough to be intendered can be measured micro-hardness of each phase. Since it depends on the composition, structure and type of processing the material, the resulting information [3], it appears useful for the study of the complex system and a contact in particular for their residual resource. This is shown in the figure 11.

Residual resource contactor elements is evaluated by comparing the slopes of the volt-ampere features of worked and non-working patterns and causes of degradation phenomena are determined by measurements of micro-hardness and phase analysis of alloys constituting the contact spots. For the
degradation determination is used: i) linear schedule in two points, and determines the rate of degradation for a period of 8 years; ii) for a basic mechanism of aging is considered diffusion of the metal atoms in the alloy in less percentage as the formation of microphases and destructure of the contactor alloy. As the main factors facilitating this process is determined: temperature, operating current and time. Almost all unused contacts have linear volt-ampere futures and close contact resistances of several $\text{m}\Omega$.

A large part of the used contactors are with linear volt-ampere characteristics but with higher contact resistances and they have additional working time. The average characteristics of both types are shown in figure 12. Similarities in the relative degradation changes of the three investigated parameters and significantly greater number of contact sites of contactors many design variations have give the reason and an opportunity to find a unifying idea to explain the underlying processes causing degradation of contactors during operation process.

### 3. Insulation materials

Electronic equipment management and control of various systems of power Units № 5 and № 6 comprising insulating material is tested for the presence of degradation processes occurring in continuous use in background controlled in sense of radiation according safety standards in NPP.
Kozloduy by different weather conditions. Selected systems are operating in continuous mode about 10 years and they have taken separate blocks containing different dielectric materials (paint coatings, substrates for printed circuit boards, cable insulation and electrical protection elements). There were measured dielectric permittivity $\varepsilon$, dielectric losses factor $\tan\delta$, and specific resistivity $\rho$ of used dielectric materials and insulators for cables of electronic equipment of NPP. The resulting values were averaged over all measured patterns and compared with available tabulated values for the specific insulating materials. The comparison is made with the table data, since it is well known that in the dielectric material was observed degradation changes in time without being subject to any real exploitation. The measurement of main parameters of the identified models is performed and analyzed by a theoretical model according to which upon degradation of dielectric and insulation materials increases the electrical conductivity at operating voltages. This is related to a change in the polarization mechanism of dielectric dipole structure or the occurrence of double injection in a dielectric, which can be considered as wideband semiconductor.
3.1 Volt-ampere characteristics

It is examines the linearity of the volt-ampere feature of the tested specimens, as the voltage is changed from about 200 to 1000V with a step of 50V. If the ratio current/voltage is not preserved, these are symptoms of several possible processes, namely: a change of the polarizing mechanism, forming conductive cords, or the occurrence of a double injection. Received data from three types are presented in figure 13a,b,c:

a) the majority (about 80%) have no strong deviations from the linear character;

b) in another group (about 10%) there are horizontal initial sections in the volt-ampere features which are offset relative to zero of the abscissa. This is an indication of the beginning of surface leakages;

c) in a third group (about 10%) are observed sections with a negative resistance at about 500V, which suggests degradation processes associated with a double injection. For the specimens of three types of defined shape and size is possible also to determine independently the dielectric loss factor by the separate measurement of the two components of the conductivity and by bridge allows operation in two modes: -direct measurement of the dielectric loss factor; -separate measurement of the capacity (for the determination of relative permittivity) and the active impedance (for possible calculating the dielectric loss factor). Preliminary comparison of the measured values with same tabular data for the discussed materials show predominantly falling within the tolerances as is shown in for example in table 1.

Table 1. Comparison of the measured values with same tabular date of dielectric.

| №  | Experimental dates ε | Material of the samples | Table dates ε | tgdδ |
|----|----------------------|-------------------------|---------------|------|
| 3  | 2.9 – 3              | vinylite                | 3.2 – 4       | 0.01 – 0.05 |
| 14 | 3.6                  | Insulation canvas       | 3 – 4.5       | 0.02 – 0.3 |
| 15 | 7                    | bakelite                | 5 – 12        | 0.02 – 0.5 |
| 16 | 14                   | ceramics                | 0.0005 – 0.025|

Figure 13. Three types of volt-ampere characteristics of dielectric materials.
Preliminary analysis of the measurements shows that the overwhelming number of cases there is an expected trend of degradation modification of the parameter, namely: reduction of dielectric permittivity and specific resistance and increase of dielectric loss factor. The fact that the relative degradation changes of the basic parameters of such a large group of diverse materials (for example is shown on figure 14 for $\tan \delta$) have similar numerical intervals shows some community of processes causing degradation. This and the results of the study of the previous two groups of components (diodes and transistors and contactors) allow the construction of a general explanation of the observed changes in the parameters of electronic components and materials in the process of operation.

4. Conclusions

From the conducted studies, it is clear that the main degradation processes in the three groups of elements for an extended period of time are slow do not lead to a hopping change in basic parameters and to catastrophic failures. This gives grounds to suggest a common diffusion model, which is limited to the following: in electronic components containing a p-n junction, is performed diffusion of residual copper atoms, that are accumulated in the area of a spatial charge under the influence of the electric field and the local temperature, creating shunt channels; in the contactor systems whose contact surfaces are made of metal alloys under the influence of increased temperature starts decompositions of a homogeneous alloy. Conditions are created for diffusion of individual atoms. to the surface, micro-phases of homogeneous atoms are formed and modify the contact resistances; in the course of time in the insulating materials are changed the mechanisms of polarization, double bonds and dipoles are disrupting, leading to the release of carbon atoms. The latter diffuse at elevated temperature and form conductive cords, which amend the dielectric losses and specific resistance of the materials.

Therefore, the total physical model of slow degradation in electronic systems can be built on diffusion processes of free atoms under the influence of local temperature and electric field. These processes are uncontrollable, their speed is slow and the time of change of the resource can be predicted by using the developed methods.
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