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C and *AC* Electron-Transport Properties of Polyimide Foils Implanted by Co^+ and Cu^+ Ions

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Abstract:

Temperature dependence of resistance in *DC* regime and *AC* electron-transport properties in thin polyimide (PI) foils implanted by 40 keV Co^+ and Cu^+ ions with fluencies range of 2.5×10^{16} to 1.25×10^{17} cm^{-2} at ion current densities of 4, 8 and 12 μA /cm^2 were studied as function of ion fluence. It was found that in the contrary cobalt implantation, when implantation by highest fluence ($1{,}25 \times 10^{17}$ cm^{-2}) at ion current density more 8 μA/cm^2 lead to insulator – to – metal transition and change impedance characteristics from capacitive to inductive, implantation by copper ions did not lead to these changes. Catalysis action of cobalt atom on graphitization processes into carbonized polymer layer as well as forming elongate labyrinth-like conductive structure at Co^+ implantation lead to insulator-to-metal transition and change impedance characteristics, whereas blocking π-electrons by copper atoms and forming spherical copper clusters in carbonized layer did not allow observe these transitions at the same regimes of implantation.

1. Introduction:-

Ion implantation is one of the effective methods to control conductive properties of polymers. In general, an increase of conductance in the ion-implanted polymers is caused by radiation-induced carbonization, formation of carbon-rich clusters with conjugated bonds and sp^2 hybridization, as well as metal atom coalescence into the nanoparticles for implantation ions of metal [1]. For the last two decades, there has been growing interest in metal ion implantation into dielectrics for nanoparticles formation. In particular DC current properties of granular thin films have been widely investigated and explained in the dielectric regime in terms of thermally assisted hopping/tunneling [2] and processes of weak localization on the metallic side of the insulator to metal transition [3]. The AC response such systems is not yet properly characterized in the limit where admittance rising from interparticle tunneling processes and interparticle capacitances become of similar magnitude [4]. In this paper we continue presenting data on the study electrical properties of polyimide implanted by magnetic and nonmagnetic ions of metals, in particular, *dc* and *ac* measurements thin polyimide films implanted by copper ions are comparison with thin polyimide films implanted by cobalt ions.

2. Exerimental.

Thin (40 μm) polyimide (PI) foils were implanted by 40 keV Co^+ and Cu^+ ions with fluencies range of 2.5×10^{16} to 1.25×10^{17} cm^{-2} at ion current densities of 4, 8 and 12 $\mu A/cm^2$ in a residual vacuum of 10^{-5} Torr. The sample holder was water-cooled and the temperature of the PI samples under implantation did not exceed 370 K, which is much lower then the PI glass-transition [5] that allowed to prevent polymer overheating and thermal degradation during the implantation. To provide ohmic electrical contacts to the implanted layer, the electrodes were deposited on the ends of the samples using conducting silver epoxy. Temperature dependence of resistance was measured in the interval of 40 - 300 K using a standard quasi-four-probe method in *DC*regime and at 300 K in *AC* regime in the frequency range of 20 Hz to 1 MHz. In order to clarify electron-transport mechanism in implanted samples temperature dependence of resistance at $\ln R - T^{-P}$ scales, where P = 1/4, 1/3, 1/2, 1 [6], as well as temperature dependence local energy for conductivity activation ln(W) = -d(lnR)/d(lnT) [7] were plotted. The measurements were carried out at voltages corresponding to linear interval of current-voltage dependence.

3. Result and discussion:-

Temperature dependences of resistance for PI implanted by Cu^+ ions in the entire range of fluences at different implantation current density are presented in Fig. 1. The resistance of the implanted samples decrease with fluence increasing because of radiation-induced carbonization and formation of copper clusters in the implanted near-surface region of carbonized polymer. Resistivity of the samples implanted by Co^+ and Cu^+ ions are listed in the table 1 for different fluences and ion current density was calculated using thickness of the conducting layer 100 nm based on the TEM and Rutherford backscattering data [8, 9]. One can see value of the resistivity for used regimes of implantation for Co^+ implanted samples decreases more then four order of value, whereas for Cu^+ implanted samples it decreases more then two order of value only. It should be mentioned that in the contrary of early results observation transition from insulating to metallic conductivity via processes of weak localization in polyimide implanted by cobalt ions [3] the slope of all curves on Fig. 1 corresponds to a negative temperature coefficient of resistance. It means that even at highest fluence and ions current density all Cu^+ implanted samples show insulating regime of conductivity (insulating side of the insulator- to- metal transition (IMT) in spite of atomic mass of copper is a little higher.

Nevertheless, since for maxima fluence and ions current density implantation resistance increase insignificantly with decreasing temperature up to 40 K (curve 4 in Fig.1), what can be deal with processes of weak localization in the regime of metallic conductivity [10], we have analyzed temperature dependence of local activation energy for conductivity presented in Fig. 2. The slope of these dependences is negative confirming insulating regime of electron transport for all regimes of implantation. On the dielectric side of the IMT the temperature dependence of resistance is typically described by well-known Mott's equation [6, 10] for variable range hopping

$$R(T) = R_0 \exp(T_0/T)^P \qquad (1)$$

where R_0 is prefactor and P is a power characterising the dimension (D) of hopping $P = 1/(1+D)$, $D = 1, 2, 3$.

The attempt to fit the "dielectric" curves on the insulating side of the IMT with one of the possible $P = 1/2, 1/3, 1/4$ or 1 for the sample implanted with fluence of 5×10^{16} cm^{-2} is shown in Fig. 3. Practically for all samples these dependences can be approximated by a linear function in coordinates $\ln(R/R_{295}) - (1/T)^{1/2}$ at temperature below 80 K. Hence, it can be suggested that at high temperatures there are few possible mechanisms contributing into the charge carrier transport while for the temperature interval below 80 K there is a dominant mechanism giving the $R \sim \exp(1/T)^{1/2}$ dependence. Such temperature dependence of resistance was theoretically predicted [10] for electrons tunnelling between metallic clusters in insulating matrix and it is typical for disordered material, in particular, for granular metals [11].

Abcense transition from insulating to metallic regime of conductivity at Cu^+ implantation, in the contrary our previous study for Co^+ implantation [3], can be deal with several reasons. In our opinion the main reason of the difference in electron-transport characteristics for cobalt and copper ions implanted polyimide is difference in chemical interaction of cobalt and copper atoms with carbon. It is well-known catalysis action of Co atoms on processes of graphitization in carbonized layer of polymer [12], while introduction copper atoms into molecular net of graphite lead to π -electrons blocking [13], in other words decreasing conductivity modified layer of polyimide. In addition, because of magnetism of Co atoms and its hexagonal crystalline structure at high-fluence implantation they form elongate labyrinth-like structure [14], while nonmagnetic copper with cubic structure – spherical nanoparticles [15]. Consequently it can be expected that infinite conductive copper cluster is formed at higher fluence. Moreover, it was shown elsewhere [16] that graphite-like conductive clusters producing at copper introducing into carbon reach the same size, compare with cobalt, at copper concentration three times higher than cobalt concentration, testify more strong interaction of cobalt atoms with carbon.

The phase shift of the voltage drop across the sample and current on frequency is shown in Fig. 4. One can see that shift is negative for all regimes of implantation and frequencies supporting absence transition from insulating to metallic regime of conductivity, when capacitive character of impedance change on inductive, as was observed early for cobalt implantation in polyimide [3] . Fig. 5. precents impedance spectrum (Im(Z)-Re(Z) – locus of impedance normalized on its maxima value) for all samples which have typical shape of semi-circle with maxima shifting from 20 to 300 kHz with fluence increasing. The maximum of the dependences corresponds to the condition □□□□□1 where □ is cyclic frequency and □ is time constant (relaxation time), for the structure "conductive inclusion - insulating layer- conductive inclusion" in the approximation of an ideal plate capacitor in RC circuit [17] . For this ideal model □~ε□εr⁄σ□ where ε_o is the permittivity □r is the relative permittivity and σ is the electric conductivity of the insulating layer, the time constant can be considered as a Maxwell relaxation time. Its values are listed in the table 1 for copper implantation and they are approximately one order of magnitude lower compare with cobalt implanted samples.

4. Conclusions.

Temperature dependences of resistance in *DC* regime and *AC* measurements of electron-transport characteristics of polyimide foils implanted by 40 keV Co^+ and Cu^+ ions with fluencies range of 2.5×10^{16} to 1.25×10^{17} cm^{-2} at ion current densities of 4, 8 and 12 $\mu A/cm^2$ have been carried out. It is shown that nucleation of the copper nanoclusters and their coalescence with increase of implantation fluence, in the contrary cobalt ions implantation, did not lead to transition from insulating to metallic regime of conductivity as well as transition from capacitive to inductive impedance characteristics of implanted samples. It is caused on the one hand by copper atoms blocking of π-electrons in carbonized polymer layer and, on the other hand, spherical shape of forming copper nanoparticles in carbonized conducting layer and that is why more high copper concentration to form infinite conductive metallic cluster.

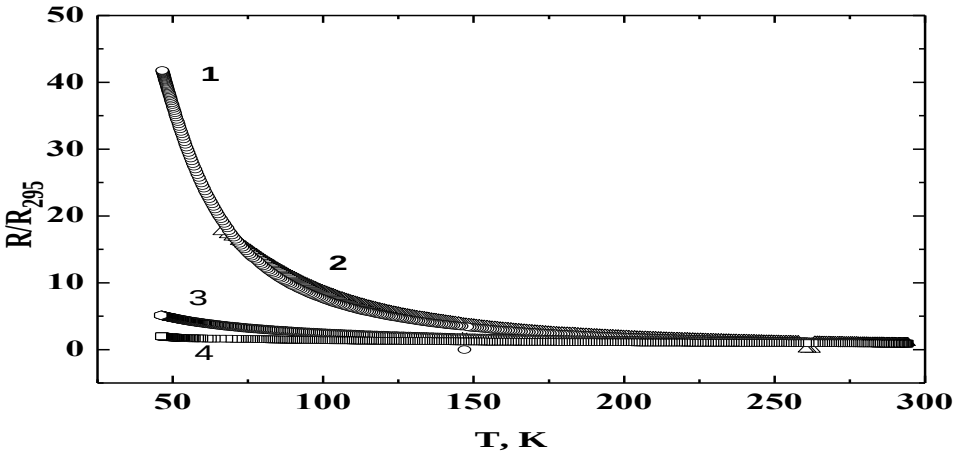

Fig.1. Temperature dependences of resistance normalized on value at room temperature for implanted samples D, см$^{-2}$: 1 – 5 × 10^{16}; 2 – 7,5 3, 4 – 1.25 ×10^{17} × 10^{16} ; . j, μA/см^2 : 1, 2 – 4; 3 – 8; 4 – 12

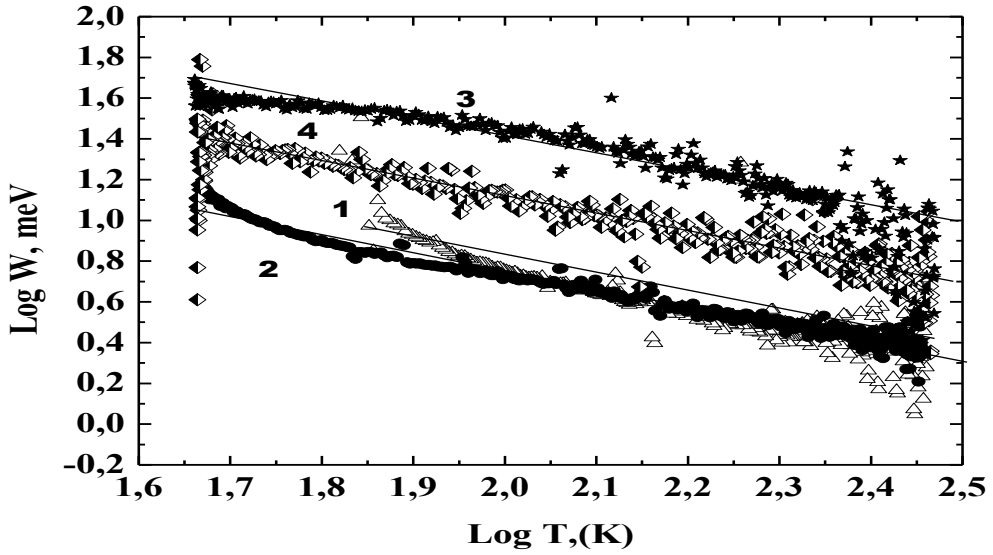

Fig.2 Dependence of local energy for conductivity activation for the same samples.

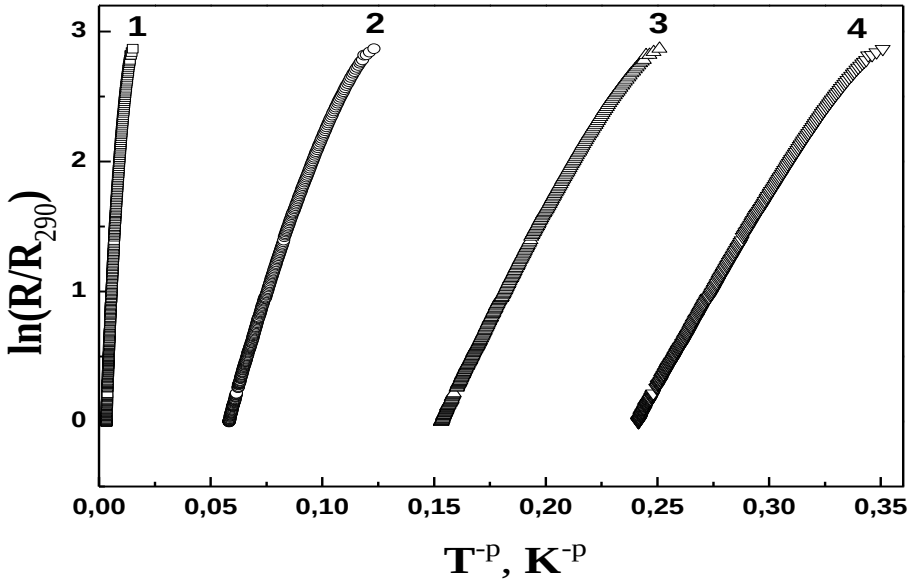

Fig. 3. Temperature dependence of resistance for sample No. 2 in $\ln R/R_{295} - T^{-P}$ scale at different exponent p: 1-1; 2 - 1/2; 3 - 1/3; 4 - 1/4.

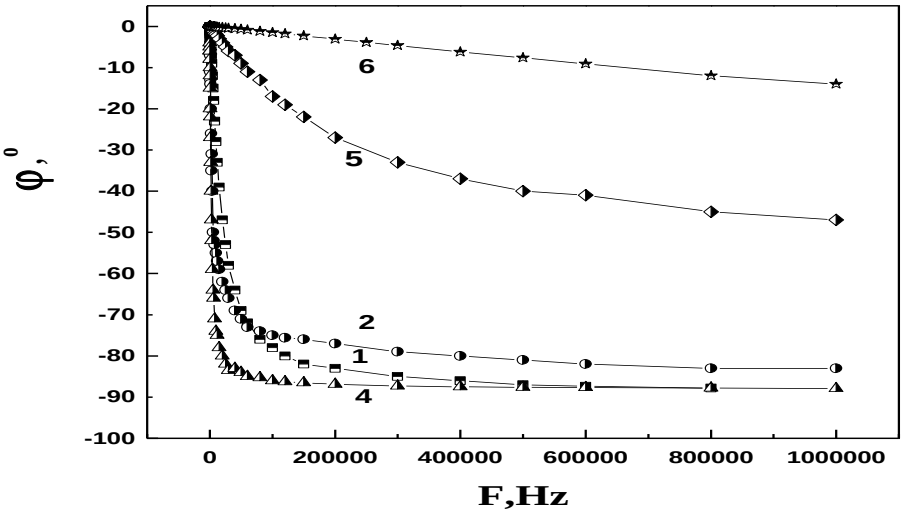

Fig. 4. Dependence of phase shift on frequency. Number of the curve corresponds number of the sample in the table 1.

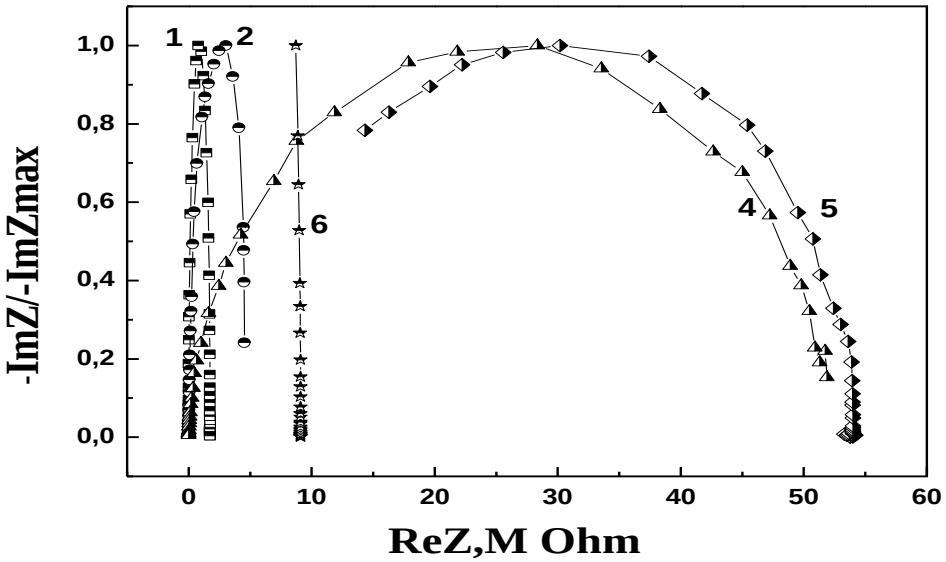

Fig. 5. Impedance spectrum for the same samples with change of frequency 20 Hz – 1 MHz.

Table 1. Specific resistance of polyimide foils implanted by Co^+ and Cu^+ ions with different fluences at different density of an ionic current.

Number of the sample	Dose, cm^{-2}	Current $\mu A/cm^2$	Resistivity, Ohm.cm Co^+	Resistivity, Ohm.cm Cu^+	Time relaxation μks
1	2.5×10^{16}	4	17.6	5,64	0.5
2	5.0×10^{16}	4	17.2	2,02	0.07
3	7.5×10^{16}	4	0.21	1,45	-
4	1.25×10^{17}	4	0.18	0,7	0,05
5	1.25×10^{17}	8	1.8×10^{-3}	0,2	8
6	1.25×10^{17}	12	7.5×10^{-4}	0,05	27

References

[1] R.I. Khaibullin, B.Z. Rameev, A.L. Stepanov, C.Okay, V.A.Zhikharev, L.R. Tagirov, and B. Atkas, in: Nanostructured Materials and their applications, edited by B. Atkas, L. Tagirov, and F. Mikailov (Kluwer, Dordrecht,), p.33. (2004).

[2] V. N. Popok, I. I. Azarko, R.I. Khaibullin, A.L.Stepanov, V. Hnatowicz, S.V.Prasalovich, Appl.Phys. A 78, p.1076 (2004)

[3] V. Popok, M. Lukashevich, S. Lukashevich, R. Khaibullin, V. Bazarov. Surface Science, 566 – 568, 327 (2004).

[4] B.J. Hatting, A. Labarta, M. Garcia del Muro, and X. Battle. Phys. Rev.B 67, (033402-1) (2003).

[5] L.A. Laius, E.N. Dergacheva, and T.J.Zhukova, in: Poliimides, chemistry and characterization, edited by C. Feger, V.V. Khojasteh, and J.E. McGrath (Elsevier, Amsterdam, 1989), p. 389.

[6] N.F. Mott, E. Devis. Electronic Processes in Non-Crystalline Materials. Clarendon, Oxford. P.664 (1979).

[7] A. Heines, M. Karpovski, M. Pilosof, M. Witcomb, R. Rosenbaum. Phys. Stat. Sol (B). – 1998. – Vol. 205. – P. 237 – 240.

[8] V.N. Popok, R.I. Khaibullin, V.V. Bazarov, V.F. Valeev, V. Hnatowicz, A. Mackova, V.B. Odzhaev.Nucl. Instrum. Meth, B191,695 (2002).

[9] V.N. Popok, R.I. Khaibullin, A. Toth, V. Beshliu, V. Hnatowicz, A. Mackova. Surface Science, 1034, 532 (2003).

[8] G. Bergman. Phys. Rep. 107, № 1, 1 (1984).

[9] Б.И. Шкловский, Ф.Л. Эфрос.Электронные свойства легированных полупроводников. М.: Наука,– 416 с. (1979).

[10] B. Abeles, Structural and electrical properties of granular metal films / B. Abeles, P. Sheng, M. Coutts, Y. Arie, Adv. Phys. ,Vol. 24. – P. 407 – 461. (1975).
[11] X. Battle, A. Labarta .J. Phys. D: Appl. Phys. 35 ,R15 (2002).
[12] J. Jiao, S. Seraphin. J. Appl. Phys. 83, 2442 (1998).
[13] V.D. Andreeva, T.P. Stepanjva. Pisma v ZTP. 28, №18, 18 (2002).(in Russian)
[14] B. Rameev, C. Okay, F. Yildiz, R.I. Khaibullin, V.N. Popok, B. Aktas. J. Magn. M Mater. 278,164 (2004).
[15] Y. V. Petyhov, M. I. Ibragimova, N.R. Khabibullina, S.V. Shulundin, Y.N. Osin, E.P. Zeglov, T.A. Vanohina, I.B. Khaibullin. Vusokomolekyliarnue soedinenia. 43, № 11, 1973 (2001). (in Russian)
[16] T.K. Zvonareva, E.I. Ivanova, G.S. Frolova, V.M Lebedev, V.I. Ivanov-Omski. ФТП. 2002. Т. 36, вып. 6.- С. 736 – 740. (in Russian).
[17] E. Barsukov and J. R. MacDonald. Impedance spectroscopy: theory, experiment, an applications (Wiley, Hoboken, 2005).

خصائص نقل الالكترون في التيار المستمر والمتناوب للبولي اميد المطعم بأيونات الكوبلت Co^+ والنحاس Cu^+

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الخلاصة:-

اعتماد درجة الحرارة على المقاومة في خواص نقل الالكترون في التيار المستمر والمتناوب لرقائق البولي اميد المطعمة بالكوبلت Co^+والنحاسCu^+ بطاقة 40 keV وبمدى تأثير جرعات 10^{16} × 2.5 الى 1.25 ×10^{17} cm^{-2}ضمن كثافة تيار ($4,8,12\ \mu A/cm^2$). لقد لوحظ العكس في حالة تطعيم الكوبلت عند الجرعات العالية(10^{17}× 1.25) وكثافة تيار($8\ \mu A/cm^2$) ادت الى تحويل العازل الى معدن وايضا تحولت خواص الممانعة من متسعة الى محاثة، اما في تطعيم النحاس فلم يلاحظ اي من هذه التحويلات والسبب في ذلك هو تحفيزذرات الكوبلت وفق عمليات (graphitization)التي تحدث في البوليمرضمن طبقات الكاربون وكذلك فضلا عن تشكيل استطالة متاهة مثل هيكل التوصيل في الكوبلت المطعم الذي تحول من عازل الى معدن والذي بدوره ادى الى تغيير خواص الممانعة، في حين تم حجب الكترونات(π) من قبل ذرات النحاس وتشكيل كتل كروية من طبقات الكاربون التي بدورها تمنع شروط الانتقال.