Journal of Advanced Materials
Volume 5, Number 1, pp. 1-6
Copyright © 1999 Nova Science Publishers, Inc.

A Simple Theory and Experimental Investigation of Ion-Assisted Deposition of Cobalt Coating on Silicon

G. Carter, J. Colligon, I. S. Tashlykov

The results of experimental and theoretical investigation of the processes of 200 and 500 eV Ar ion-assisted cobalt coating deposition on silicon have been presented. The rate of cobalt coating deposition, R_d, on different samples varied from 3.5 to 10^{15} at (cm^2s). The measured ratio of ion current density, J_j to R_d ranged from 0.1 to 0.9 ion/atom. It is shown that due to the sputtering effect the cobalt deposition rate R_{Co} tends to zero at $(J/R_d)>0.7$. The dependence of deposited thin cobalt film thickness at ion-assisted coating deposition (IACD) on the J_j/R_d ratio and Ar ion energy is established. The coefficients of cobalt sputtering and Ar trapping by coating are determined experimentally. It is shown that in the studied 200-500 eV internal the interpenetration of the components is sufficiently influenced by Ar^+ ions energy whose increase contributes to the broadening of the mixed layer at the phase interface region. An elementary theory is suggested that makes it possible to simulate the IACD process taking into account the effects of surface sputtering and trapping of assisting gas by coating.

Introduction

In vacuum technologies of coating deposition on materials and products, or practical interest are the methods, which combine coating deposition with ion bombardment [1-2]. Irradiation of a formed coating/substrate structure by ions of inert (as a rule) or chemically active gases can lead to creation of a desired composition and structure of the coating, its absolute adhesion to the substrate as a result of interpenetration of matrix and coating components at the interphase border [3-5]. Though it is know that in this process the inert gas atoms are trapped by the coating [6,7], there are very scarce quantitative data on their distribution in depth and on the influence of IACD parameters on gas distribution and concentration. In this work, experiments on thin cobalt coating deposition on silicon have been carried out using a controlled ion-beam system providing controlled J_j/R_d ratio and required energy of assisting Ar^+ ions. The elementary composition of the coatings and interphase area are studied experimentally as well as the influence of argon ions and regimes of coating deposition on their composition and interpenetration of the components.

РЕПОЗИТОРИЙ БГПУ

Experiment

Cobalt coatings on silicon were applied by means of a system described in [1] in which two Ar ion sources of the Kaufman type were used. One of them created an Ar^+ ion beam with E=1 keV for the Co plate sputtering which at the given experimental geometry made it possible to deposit cobalt on four silicon substrates in one run with deposition rate in the range from 3.4 to $10.2\cdot10^{14}$ at/$(cm^2\cdot s)$. The other ion source was used to produce Ar^+ ions with E=200 or 500 eV which were utilized for ion assisting deposition of thin cobalt film deposited on silicon samples. Ion current density was controlled by eight Faraday cups – two for each of the substrates covered by cobalt, the substrates being placed between the cups. Thus, the experimental conditions provided controlled J_j/R_d ratio in the range from 0.1 to 0.9. The base pressure in the chamber was ~10^{-7} Torr. However, during the experiment, due to inleakage of argon in both ion sources it increased up to ~$2\text{-}3\cdot10^{4}$ Torr. The vacuum quality (spectral composition) was controlled by a quadruple mass-spectrometer. During the coatings deposition the target temperature measured by thermocouples built in the holder was constant 330-350 K.

Layer-by layer elementary composition of the Co/Si structures, the rate of passive Co deposition, the processes of cobalt sputtering, argon trapping at ion assistance, component interpenetration depending on the IACD regime were studied by means of the Rutherford back scattering (RBS) of helium ions with E_o=2.0 MeV using known methods [8]. The geometry of the experiments was as follows: scattering angle =168 , entrance angle $_1$=0 and $_2$=12 . Energy resolution of the system was E=25 keV, channel energy width was E=5 keV. Experimentally produced back scattering (BS)

spectra of helium ions were also simulated using the computer software RUMP [9].

RESULTS AND DISCUSSION

Spectroscopy of Rutherford ion back scattering in combination with selected regimes of coating deposition when the signals on the BS spectra do not overlap provides a valid quantitative information of layer concentration as well as on component distribution throughout the thickness of each coating deposited on silicon. Fig. 1 shows experimental BS spectra obtained at argon assisted (E_{Ar}=500 keV) deposition of cobalt on silicon. In addition to the signals from silicon and cobalt within the range of 230-270 channels, the BS spectra show signals from argon trapped by the coating in the process of cobalt deposition as was mentioned elsewhere for other systems [5-7]. The character of the cobalt and argon signals suggests rather uniform distribution of argon throughout the thickness of cobalt thin film. Only when (J_i/R_d) 0.29 and film thickness u to ~100 nm there appears a tendency of the Ar concentration increase at the film/substrate interface and on the coating surface, curve 4, Fig. 1. the relative values of layer concentrations of argon in the cobalt coating $(Nt)_{Ar}/(Nt)_{Co}$ as well as the IACD regimes are presented in Table 1.

Table 1

Regimes of ion-assisted deposition of cobalt coating on silicon and the values of relative concentration of argon trapped by the cobalt film, argon trapping coefficients

R_d 10^{14} $cm^{-2}s^{-1}$	$(Nt)_{Ar}/(Nt)_{Co}$%	E_{Ar}=200 eV				E_{Ar}=500 eV			
		J_i 10^{14} $cm^{-2}s^{-1}$	J_i/R_d	R_{Co}/R_d	$(Nt)_{Ar}/(Nt)_{Co}$ %	J_i 10^{14} $cm^{-2}s^{-1}$	J_i/R_d	R_{Co}/R_d	$(Nt)_{Ar}/(Nt)_{Co}$ %
3.4	0.23	0.91	0.27	0.64	1.1	3.1	0.91	<0.02	2.9
4.9	0.22	0.91	0.19	0.74	0.9	3.4	0.71	0.04	2.8
7.0	0.22	0.90	0.13	0.76	0.9	3.3	0.48	0.33	2.8
10.2	0.22	0.81	0.08	0.71	0.7	2.9	0.29	0.50	2.1
η	-		0.15				0.26		

It should be noted that within the range of 340-370 channels in the BS spectra, Fig. 1, there are small peaks that are identified as tungsten and palladium "traces" in the cobalt film. The concentration of these concomitant impurities in the thickness of the deposited coating is constant ranging from 0.05 to 0.5 at %, and their emergence in the coating may be due to the processes of secondary back sputtering of the fixing components in the vacuum chamber and passive deposition onto all the units in the chamber, including silicon substrates.

Therefore, it can be stated that IACD of cobalt onto silicon is accompanied by the processes of coating deposition on the substrate, irradiation of the formed structure resulting in mixing of the components, surface sputtering, trapping of assisting argon, etc. To describe these processes, an attempt has been made to develop a simple theory of IACD taking into consideration the effects of surface sputtering and trapping of the assisting gas by the deposited coating. In this case, unlike the authors of [10], who set and solve differential equations describing absorption, subplantation, sputtering, cascade mixing, our model presents a generalized consideration of the IACD process.

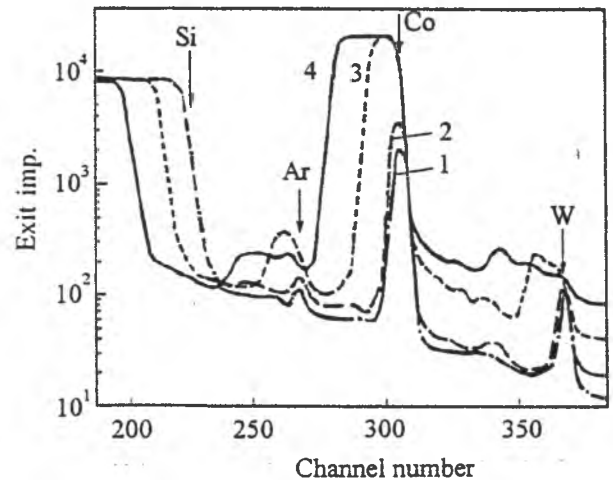

Fig. 1. Energy spectra of BS He ions with E_o=2 MeV from the Co/Si structure obtained using IACD, E_{Ar}=500 eV, J_i/R_d: 1-0.91; 2-0.71; 3-0.48; 4-0.29

РЕПОЗИТОРИЙ БГПУ

It is assumed that following the initial period of growth of the coating when its thickness is comparable with the penetration depth of recoil atoms (cobalt) driven into silicon by argon ions, the coating deposition process becomes stabilized. An equilibrium is established at which there is a constant relation between the rate of Ar^+ ions trapping and sputtering of argon atoms from the near surface area of the growing film. In these conditions, with growth of the coating the argon concentration $(Nt)_{Ar}$ and cobalt concentration $(Nt)_{Co}$ become independent of the surface position which is confirmed by the character of signals from Ar and Co in Fig. 1. Other parameters (for instance, density) of the coatings formed by the IACD method are also saturated and remain constant throughout the whole thickness [11].

If we designate the coefficient of surface sputtering at the coating growth as Y, and the probability of argon trapping as , the following equations can be applied describing the film growth rate R_{Co} under the conditions of the IACD process:

$$R_{Co} = R_d - J_i Y \quad (1)$$

and calculation of the layer concentrations of cobalt and argon in the coating:

$$\frac{(N_t)_{Co}}{(N_t)_{Ar}} = \frac{R_{Co}}{R_{Ar}} = \frac{R_d - J_i Y}{J_i \eta} \quad (2)$$

where R_{Ar} is the rate of argon trapping by the coating.

Equation (1) can be rewritten in the form convenient for the analysis:

$$\frac{R_{Co}}{R_d} = 1 - \left(\frac{J_t}{R_d}\right) Y \quad (3)$$

while equation (2) can be rewritten in the form:

$$\frac{(N_t)_{Co}}{(N_t)_{Ar}} = \left(\frac{R_d}{J_i} - Y\right)\frac{1}{\eta} \quad (4)$$

As a result analytical expressions (3) and (4) were obtained appropriate for determination of dependence of the coating parameters on IACD regimes. Thus, according to (3), the R_{Co}/R_d ratio should be a linear function of J_i/R_d with the coefficient Y. Also $(Nt)_{Co}/(Nt)_{Ar}$ should be a linear function of the $(R_d/J_j - Y)$ ratio with the coefficient 1/ . Since R_{Co}, R_d, $(Nt)_{Co}$, $(Nt)_{Ar}$, and J_j are values measured in the experiment, then equation (3) makes it possible to determine the effective coefficient of cobalt sputtering in the deposited coating. As to the coefficient of assisting gas trapping by the coating, it is calculated at constructing a corresponding dependence on the basis of equation (4).

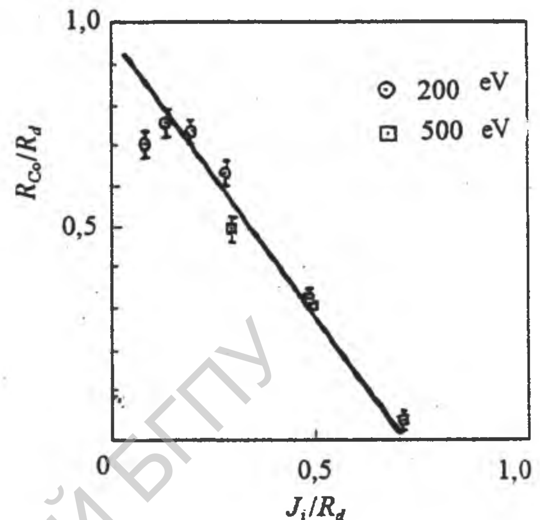

Fig. 2. Dependence of the relative rate of cobalt deposition on silicon on the J/R_d parameter

Fig. 2 shows the dependence of the relative rate of cobalt deposition on the parameter J_i/R_d. According to equation (3), within the experimental accuracy this rate is, indeed, a linear function of J_i/R_d. The deviation of the value R_{Co}/R_d from the linear dependence at the lowest J_i/R_d ratio may be partially associated with the fact that fast neutral argon atoms scattered from the sputtered Co plate hit against the deposited coating of the sample located closer to the plate (with maximum R_d) thus making an additional and uncontrollable contribution to the coating sputtering.

The corresponding common dependencies of the values of the points as shown in Figure 2 turned out to be somewhat unexpected. These were obtained in experiments with various energies of the Ar ion-assisted. For example, in accordance with the data of [12] we have Y(200 eV) = 0.5, a Y(500 eV) = 1.1 at./ion. The value of the coefficient of sputtering obtained experimentally in this research consisted of 1.5 at./ion. So the essential nonagreement of the experimental and the theoretical values of Y can be connected, obviously, with various structures in the deposited films and in the cobalt mass.

We note also that the essential effect first of all for the technology of the ion assisting comes from the direction of the dependencies shown in Figure 2. Therefore, if the value of J_i/R_d achieves or exceeds .07, then the relative speed of the sputtering of the cobalt

РЕПОЗИТОРИЙ БГПУ

strives towards 0. This effect is connected with the almost complete sputtering of the deposited coatings of the ion-assisted argon. The characteristic of the signals on the spectrum OP from Co in the region of 290 – 315 channels, lines 1 and 2, Figure 1, testify that in the quality of coatings sputtered in such conditions, it is possible to examine the pre-surface region of the substrate with the interior of it as a result of the atomic induction with radiation by cobalt and argon. The obtained critical values J_iR_d satisfactorily agree with the works given [13] in which the computer modeling was carried out of the ion-assisted sputtering of metallic coatings.

The course of the curves in Figure 3 constructed on the basis of experimental data correspond with the predicted lines of $(R_d/J_i\text{-}Y)$ of the dependencies of the functions $(Nt)_{Co}/(Nt)_{Ar}$ in correspondence with Equation (4) since for the energy of the assisted ions is 200 thus and 500 eV. A somewhat larger inclination of line of the curve *l* and curve 2 on Figure 3 corresponds with that V coefficient of the trapped argon in the coating with the energy of the ions Ar^+ 200 eV less than at the energy at the E_{Ar}=500 eV. In reality, the calculation of the value of η under two different conditions shows that η (200 eV) equals 0.15, when as η (500 eV) equals 0.26, which is reflected in the tables shown above. Establishing of an increase in η (500 eV) over η (200 eV) is completely understandable insofar as it is learned [14] that with an increase in the edge of the ions, the depth of the penetration of the ions and the probability of their built-in structure of the radiation of the specimen is increased.

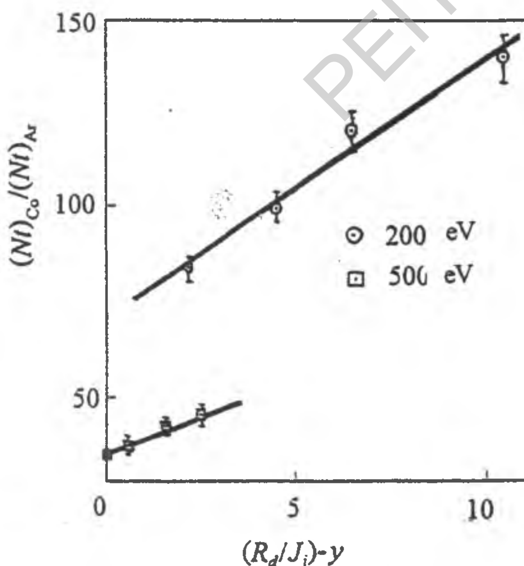

Fig. 3 Dependency of the relation of layer concentration of the upset cobalt to the argon entrapped on the coating on the parameters IANP R_d/J_I

With modeling of the IANP of cobalt on silicon with the application of the TRIM [15] program, it was concluded that the projected run and the straggling run of the ions of Ar^+ lift E = 200 and 500 eV in silicon which differs insignificantly and comprises ~ 2 and ~ 1 nm, respectively. Together with this, the carrying out of the experiment showed that in the studied interval the energy of the assisted ions of argon appears to be an important parameter for the management of the thickness of the layer on the boundary of the border of the phase film/substrate in which mutual penetration occurs of the components of the materials on the film and the substrate. The distribution of the components on the structure of Co/Si, is shown in Figure 4, which was obtained in the experiments with various energies of assisted ions of Ar. If the phase of the layer is determined in the capacity of the dispersion in the boundary of the borders in which the concentration Sl and Si are equal to 20 and 80 AT. %, then it turns out that with E_{Ar} = 200 eV, the thickness of the dispersion layer Δz_1 comprises the ~ 19 mm, and with that same E_{Ar} = 500 eV, we have Δz_2 equal to ≈30 mm. Thus these values differ approximately 1.6 times, although R_p and ΔR_p, as has been noted above, for both energies are equal and less in quantity than Δz_1 and Δz_2. Insofar as management of the cascades in which the atomic dispersion occurs are comparable to two energies and compose a section of the center of the nucleus in nanometers, then the quality of one of the fundamental mechanisms for the formation of thick (tens of nanometers) of the layers with a high concentration of components, it is possible to examine the radiation stimulation diffusion. With this we pay attention to the rather intensive flow of atoms not on the silicon on the volume of the upset coating. Therefore, we propose to actually evaluate in the future the contribution of the mechanism of atomic dispersion in the cascades of atomic collisions on the processes of developing diffusion in silicon in an upset thin films with IANP. Apparently, the intensity of the processes of mutual penetration to cobalt and the silicon also depend on the elastic stress on the boundary of the phase borders, the role of which is discussed in [16]. In this case it is obvious that the assisted upsetting of the cobalt on the Si of ions of Ar^+ with E = 500 eV, must be carried out toward the formation of a more stressed condition in the region of the boundary of CoSi. It will be interesting to represent and carry out direct measurements of the increase in the stress of the structure of CoSi obtained under varying conditions.

РЕПОЗИТОРИЙ БГПУ

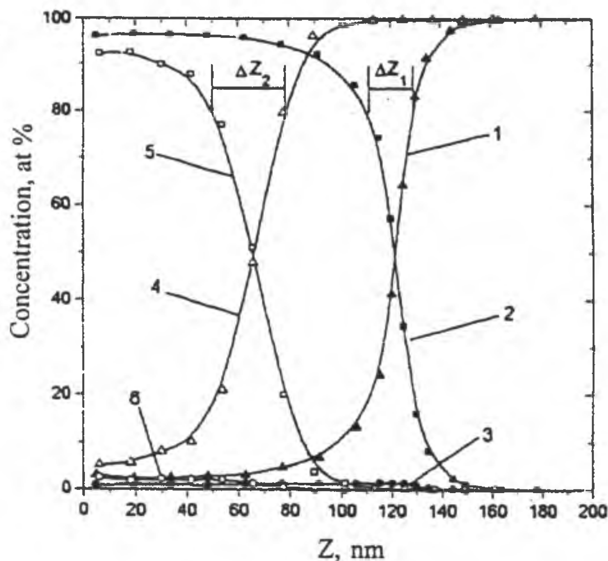

Fig. 4 Profiles of the distribution of the components in the Co/Si structures obtained with IANP: 1 and 4 - Si, 2 and 5 – Co, 3 and 6 – Ar. 1,2 and 3 – E_{Ar} = 200 eV, J_I/R_d = 0.29, R_{Co}/R_d = 0.52; 4, 5 and 6 - E_{Ar} = 500 eV, J_I/R_d = 0.48, R_{Co}/R_d = 0.35.

Restoration of the spectrum OP of helium ions with the structure of CoSi with the application of the RUMP [9] program shows that carbon and oxygen enter in the composition of all studied coating specimens which are relatively not large and reach 1-3 AT.%. The data about the content of the sputtering of argon in upset coatings obtained with modelling of their composition and application of the RUMP program verify the value of the concentration of the components which were obtained with working of the experimental spectrum of OP by well-known methods [8].

CONCLUSION

The simple theory is developed for ion-assisted deposition of coatings, taking into account the dynamic processes of upsetting and sputtering in the modification of the surfaces trapped the mixture of assisted gases. The results of the experimental research of the upsetting of cobalt on silicon with radiation-assisted ions of argon within the energies of 200 or 500 eV show a satisfactory agreement with the theoretical predicted dependencies of the relative speed of the upsetting on the parameter J_I/R_d with relation to the layers of the concentration of cobalt and the trapped argon and the coatings on the parameters R_d/J_I. With this the possibility appears to determine the effective coefficient of the sputtering of cobalt with the upset coating which comprises ~ 1, AT./ion, as well as a coefficient for the trapping of argon which changes from 0.15 with E_{Ar} = 200 eV at 0.26 when E_{Ar} = 500 eV. The IANP technology was experimentally verified elsewhere [13] with the effect of the ion-assisted when the values $(J_I/R_d) \geq 0.7$ of the relative speed of the upsetting of the covering head toward 0. It is shown that the energy of the assisted ions appears as an important parameter for the management of the measurements of the interphase boundaries, the region of which the mutual penetration of the components of the materials of the substrate and the coating, assuring the adhesion of the latter on the atomic level. With this a relatively large concentration of materials is observed on the substrate in the coating of the results of the process arising from diffusion of atom of silicon during the upsetting of the cobalt layer.

The authors are grateful to the Korolevskiy Society for financial support towards carrying out these experiments.

РЕПОЗИТОРИЙ БГПУ

REFERENCES

1. Colligon, J.S., J. Vac. Sci. Technol., 1995, v. A13, p. 1649-1657.
2. Wolf, G.K., J. Vac. Sci. Technol., 1992, v. A10, p. 1757-1764.
3. Tashlykov, I.S., Slesarenko, O.A., Colligon, J.S., Kheyrandish, H., Surf. J. Intern., 1986, v. 1, p. 106-107.
4. Faizrahmanov, I.A., Haibulin, I.B., Poverhnost, 1994, No. 10-11, p. 57-61.
5. Colligon, J.S., Kheyrandish, H., Vacuum, 1989, v. 39, p. 705-710.
6. Tashlykov, I.S., Belyi, I.M., Bobrovich, O.G., Kalbitzer, S., Meyer, O., Wolf, G.K., Enders, B., Nucl. Instr. and Methods in Phys. Res., 1993, v. B80/81, p. 98-101.
7. Ensinger, W., Thin Solid Films, 1996, v. 275, p. 54-61.
8. Komarov, F.F., Kuhmanov, M.A., Tashlykov, I.S., Nerazrushayushchi analiz poverhnostay tverdih tel ionnimi puchkami, Minsk: Belorussian State University, 1987, 257p.
9. Doolittle, L., Nucl. Instr. and Methods in Phys. Res., 1985, v. B9, p. 344-349.
10. Volokonskaya, A.A., Teplov, S.V., Poverhnost, 1994, No. 12, p. 31-39.
11. Carter, G., J. Phys. D: Appl. Phys., 1994, v. 27, p. 1046-1055.
12. Matsunami, N., Yamamura, Y., Itikawa, Y., Itoh, N., Kazumata, Y., Miyagawa, S., Morita, K., Shimizu, R., Tawara, H., IPPJ-AM, 1983, v. 32, p. 87.

13. Valdner, V.O., Zabolotny, V.Y., Starostin, E.E., Phizika, i Himiya obrabotki materialov, 1996, No. 4, p. 9-13.
14. Carter. G., Armour, D.G., Donnelly, S.E., Ingram, D.C., Webb, R.P., Rad. Effects, 1980, v. 53, p. 143-151.
15. Ziegler, J. F., Biersack, J.P., Littmark, U., In: The Stopping and Range of Ions in Solids, New York: Pergamon Press, 1985, 321p.
16. Martynenko, Yu.V., Carter, G., Rad. Effects and Defects in Solids, 1994, v. 132, p. 103-118.

ABOUT THE AUTHORS

George Carter *– Salford University (England) Professor, Doctor of Philosophy. Specialist in the field of ion-atomic processes in the interaction with irradiation by accelerated ion materials.*

John Colligon *– Salford University. Professor, Ph.D. . Specialist in the field of processes in ion-assisted deposition of coatings and modification of material properties.*

Igor Serafimovich Tashlykov *– Belorussian State Technical University. Professor, Doctor of Physico-Mathematical Sciences. Specialist in the field of modification and research of materials with application in ion-irradiation technology and nuclear physics methods.*

РЕПОЗИТОРИЙ БГПУ