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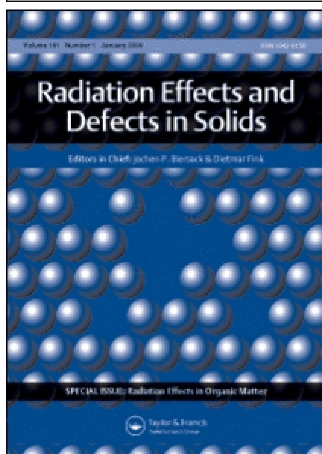

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Analysis of the composition of Ti-based thin films deposited on silicon by means of self-ion assisted deposition

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The composition of Ti-based thin films deposited on silicon using a self-ion assisted deposition (SIAD) method was investigated by utilising the Rutherford backscattering spectrometry technique and RUMP simulation code. The hydrogen affinity of the coatings produced by means of SIAD was investigated using the $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear resonance reaction. The titanium–based films on silicon were found to have a high content of oxygen, carbon, hydrogen and substantial concentration of the substrate. Near 10% H content enrichment was found at the surface of coatings but no hydrogen enrichment at the coating–substrate interfaces was observed.

Keywords: Ti-based films; Hydrogen content; Self–ion assisted deposition

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1. Introduction

Coatings of materials are widely used to provide functional, protective or decorative layers. Among the various vacuum methods, improved adhesion of a thin film generally results if additional energy is provided during the growth process as, for example, in ion–beam assisted deposition techniques [1, 2]. These methods usually have the disadvantage that the resulting coating can contain several percent of the noble gas species which may agglomerate at the film–substrate interface to form even higher local gas concentrations [2–4]. Clearly the use of ion species which are the same as the coating material would alleviate this problem and such methods are being developed [5–7]. In all of these studies, a very simple source of film species ions was used. Inevitably such a source will also produce contaminant species. For example, metal-based layers deposited on rubber by means of self-ion assisted deposition (SIAD) at 20 keV consist of metal, carbon, oxygen, hydrogen derived from the residual vacuum, vacuum oil and sulphur and zinc from the rubber surface [8, 9]. These films have scientific interest and practical significance. They have controlled adhesion between the rubber and the film

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and offer a substantial reduction in friction force against a rotating steel shaft and a sliding steel pin under non-lubricating conditions [8]. Deposition of metal-based films changes the wettability of the modified rubber surface [9]. As well as the composition of the coating, the hydrogen in the coating, and at the coating–substrate interface is one of major technological and fundamental interest. Almost no experimental data are available on the hydrogen affinity in deposited coating/substrate structures. The present work describes preliminary results from applying the SIAD system for production of titanium films on silicon.

2. Experimental

The system employed for the coating deposition has been described in detail elsewhere [9] and consists essentially of a vacuum chamber pumped by a diffusion pump to which is attached a resonance vacuum arc source (RVAS) with titanium electrodes to produce a mixture of Ti atoms and Ti^+ ions. The silicon wafer substrates were floated to a negative potential with respect to the source of 3–7 kV to accelerate the ion species. The SIAD system was pumped by a conventional diffusion pump and attained a base pressure of 10^{-2} Pa during film deposition.

The relative ratios of ions (I) to neutrals (A) could be changed between 0.1 and 0.3 by varying the parameters of the RVAS. Measured film deposition rates were between 0.6 and 1.2 nm/min. Note that the film growth rates are so low in this study because of the role of self-sputtering which is a significant factor at the ion energies used.

The composition of the deposited films was investigated using Rutherford backscattering spectroscopy (RBS). The energy of the He^+ ions was 2.0 MeV and the energy resolution of the analyzing system was 25 keV. RBS data for concentration against depth were compared with data from the RUMP (Rutherford modeling program) code simulation [10].

The H measurements were carried out by using the sharp resonance (R) of $\Gamma = 1.86$ keV occurring at $E_R = 6.385$ MeV of the $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction [11]. The targets, inside a cold shield, were placed in a cryogenic holder operating in the temperature range between 20 and 40 K. The $^{15}N^+$ beam, collimated to an area of $1.5 \times 2\,mm^2$, had an intensity of 60–200 nA.

The spectra of γ-quanta with energy in the interval 3.9–4.7 MeV were recorded using a $0.25 \times 0.25\,m^2$ NaI detector in the automatic energy scanning mode of the Heidelberg accelerator equipped with a beam deflection system based on the design of Amsel [12, 13]. In order to determine the absolute H coverage in the films a standard calibration of the system was used [14]. The conversion of the nitrogen ion energy into a depth scale was done using a ^{15}N stopping power of 1.2–1.3 keV/nm, as obtained by the computer code TRIM [15] applied to a coating having the composition estimated from the RBS measurements.

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3. Results and discussion

The information on the composition of the coatings deposited on Si at a mean rate of 0.7 nm/min during 4 h under self–ion bombardment by Ti^+ ions at 7 keV was evaluated using RBS. The RBS analysis of film composition (shown in figure 1) indicates that the deposited thin layer has a multi-component structure. It is estimated that the Ti deposition using the SIAD process is accompanied by the appearance in the coating of carbon, oxygen and silicon. The RUMP simulation of the coating composition indicates that there must also be a significant quantity of hydrogen in the film. This cannot be detected by RBS. But unless significant quantities of H are present in the films, the as-measured RBS data cannot be fitted

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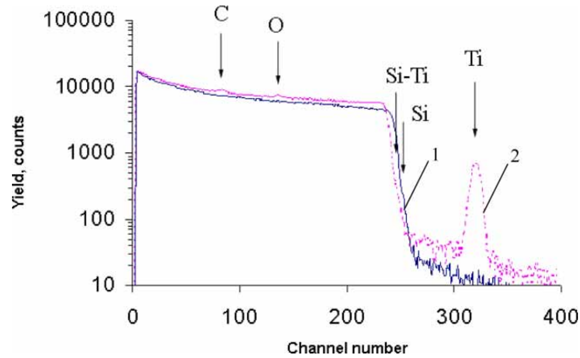

Figure 1. RBS spectra of untreated Si – curve (1); and with deposited Ti-based thin film – curve (2).

by a RUMP simulation for all the other measured component peak intensities. A complete concentration – depth profile for a sample having Ti, carbon, oxygen, silicon and hydrogen has been obtained from the original spectra using a standard computer program [10] and predicts that the Ti–based film thickness is 150–170 nm. Figure 2 indicates that the Ti concentration decreases from the top surface of the coating to a value ~50% lower near the Ti/Si interface. The titanium 'tail' in silicon as seen in figure 2 indicates that Ti atoms penetrate deep into silicon during the SIAD process, probably, because of the influence of the high energy density deposited into collision cascades [5, 16]. The hydrogen level in the coating follows an exactly similar trend, which suggests that there is at least some combination of hydrogen with Ti to form a hydride. The carbon and oxygen levels show an increase near the coating/Si interface.

It is also clear from the RBS data that there is a significant out-diffusion of Si from the substrate into the coatings, stimulated by the self–ion irradiation. The Si content falls slightly toward the surface. The driving force for the significant out-diffusion of Si atoms into the coating is, probably, the same as for penetration of Ti atoms into silicon, namely the high-energy density deposited in the collision cascades. In such circumstances, a shock wave created in the thin film/substrate system during relaxation of thermal spikes can promote inter-diffusion of the coating/substrate species [17].

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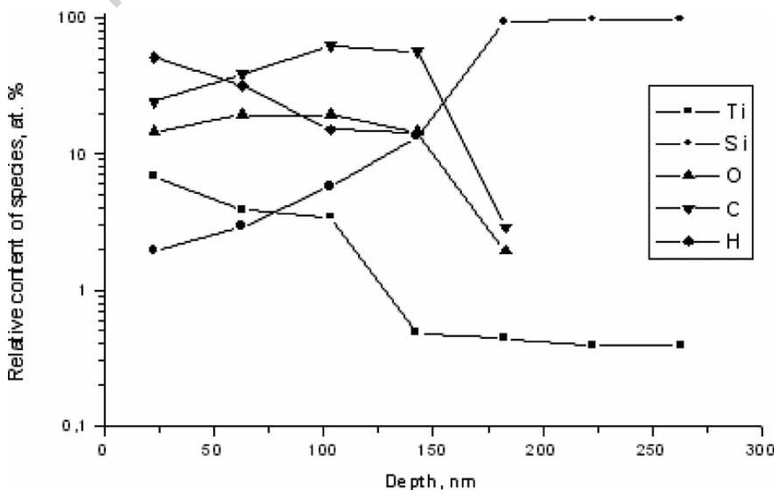

Figure 2. Relative content of species in a SIAD Ti-based thin film on Si (4 h deposition).

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The high O, C and H contents arise probably from the vacuum conditions used which allow deposition of oxyhydrocarbons onto the growing film and accumulation of them during irradiation by the accelerated Ti^+ ions. We may consider the films created by SIAD as films, the composition of which may be compared with that of solid lubricant films [18].

On the other hand it is known [14] that, when one uses the nuclear resonance reaction, there is no way of distinguishing ^{1}H from ^{1}H bearing compounds, say H_2O. Thus a measured amount of ^{1}H could also mean the presence in the coating of compounds such as H_2O or CH_3OH.

Nuclear reaction analysis was used to obtain direct measurements of the distribution and concentration of hydrogen in the same samples which were used for RBS. During this analysis, the sample was cooled to ~20 K to hinder ion–induced outgassing from the sample. The experimental results are shown in figure 3. They confirm the RBS–RUMP data about the huge amount of hydrogen in the Ti-based coatings as prepared by means of SIAD. This result is in agreement with Vistrom *et al.* [19], where it was shown that evaporated films of a variety of metals may contain concentrations of ^{1}H many orders of magnitude greater than its bulk solubility. The high concentration of ^{1}H in Ti–based films may serve as evidence that the films contain large concentrations of ^{1}H traps. The traps may be associated with grain boundaries, they may also be voids. It is known [20] that the difference in the behaviour between thin films and bulk materials may be connected with the elastic coherence of the two structures at the interface in a layered system. A lattice expansion usually accompanies hydrogen uptake.

In the depth distribution of ^{1}H in coatings one observes hydrogen enrichment in the top surface (after the first sweep of the ^{15}N beam). This result is in good agreement with the RBS – RUMP data (figure 2). However, the ^{1}H enrichment almost disappears under the influence of the analyzing beam. After the fifth sweep, the H amount of the layer is seen to decrease to 6–7%. This feature may be interpreted as a release of those hydrogen atoms which do not form any bonds with the other elements in the coatings. In the region corresponding to the thin film–Si interfaces we do not observe any hydrogen enrichment in the Ti–based coatings. This fact and the observed relatively thin ^{1}H tail (~250 Å) from the coatings into the silicon provide an indication of low defect densities at the coating–silicon interface. Otherwise, hydrogen is known [21] to be trapped in vacancies and has therefore to be distributed deeper in Si, similarly

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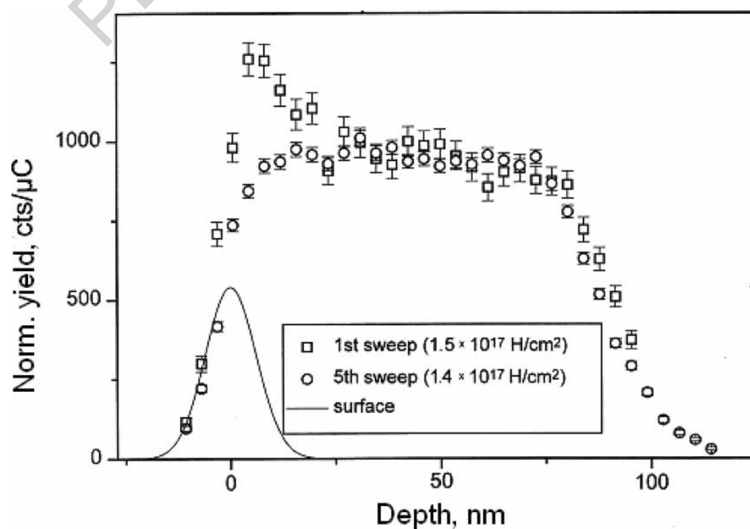

Figure 3. H content in a SIAD Ti-based layer, deposited onto Si (2 h deposition).

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to the distribution of Ti in silicon, figure 2. Indeed in our recent experiments [22], we observed that the damage of the Si surface appears to be quite small and shallow when 3 keV Ti^+ ions are used as the assisting beam in the SIAD process.

In fact there is some discrepancy in the depth scales in figures 2 and 3. This is connected with the different times taken for the deposition of the coating.

4. Conclusions

We have shown that Ti–based coatings produced by means of SIAD have a multi-component structure. Thin films deposited on silicon consist of Ti, C, O, Si and H. The high content of C, O and H arises, as we suppose, the poor vacuum used which allows the capture of oxyhydrocarbons onto the growing film and accumulation of them under irradiation by the accelerated Ti^+ ions. Silicon appears in the coatings due to an out-diffusion process from the bulk. Both the deep penetration of Ti atoms into silicon and the appearance of Si atoms in coatings are attributed to radiation-enhanced diffusion processes during SIAD of thin titanium-based films on silicon.

RBS–RUMP and NRA techniques provide comparable and adequate information about concentration and depth distributions of the hydrogen affinity at the coatings from the top surface to the coating–silicon interface.

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References

[1] G.K. Wolf, J. Vac. Sci. Technol. **A10** 1757 (1994).
[2] J.S. Colligon, J. Vac. Sci. Technol. **A13** 1649 (1995).
[3] G. Carter, J. Colligon and I.S. Tashlykov, J. Adv. Mater. **5** 1 (1999).
[4] W. Ensinger, Thin Solid Films **275** 54 (1996).
[5] I.S. Tashlykov, I.M. Belyi, O.G. Bobrovich *et al.*, Nucl. Instrum. Methods **B80/81** 98 (1993).
[6] I.V. Gusev, A.A. Mochnyuk, V.I. Chaplyuk *et al.*, Appl. Surf. Sci. **91** 182 (1995).
[7] R. Wang, Vacuum **52** 315 (1999).
[8] I.S. Tashlykov, V.I. Kasperovich, M.G. Shadrukhin *et al.*, Surf. Coat. Technol. **116–119** 848 (1999).
[9] I.S. Tashlykov, A.V. Kasperovich and G.K. Wolf, Surf. Coat. Technol. **158–159** 498 (2002).
[10] L. Doolittle, Nucl. Instrum. Methods **B15** 227 (1986).
[11] K. Izsak, S. Kalbitzer, M. Weiser *et al.*, Nucl. Instrum. Methods **B33** 578 (1988).
[12] G. Amsel, E. Artemare and E. Girard, Nucl. Instrum. Methods **191** 189(1981).
[13] M. Zinke-Allmang, V. Kössler and S. Kalbitzer, Nucl. Instrum. Methods **B15** 563 (1986).
[14] S. Jan, S. Kalbitzer, P. Oberschachtsiek *et al.*, Nucl. Instrum. Methods **B85** 321 (1994).
[15] J.F. Zigler, J.P. Biersack, U. Littmark (Editors), *The Stopping and Range of Ions in Solids*, volume 1 (Pergamon Press, Oxford, 1985), p. 321.
[16] I.S. Tashlykov and O.G. Bobrovich, Vacuum **78** 337 (2005).
[17] Yu. V. Martynenko and M.V. Umansky, Rad. Effects Defects Solids **132** 31 (1994).
[18] Y. Pauleau (Editor), *Materials and Processes for Surface and Interface Engineering*: (Kluwer Academic Publishers, Netherlands, 1995), pp. 475–527.
[19] R.E. Vistrom, P. Brgesen and S.L. Sass, Acta Metall. Mater. **41** 3549 (1993).
[20] A. Waidinger, D. Nagengast, Ch. Rehm *et al.*, Thin Solid Films **275** 48 (1996).
[21] B. Hjörvarsson, A. Stierle, G. Song *et al.*, Vacuum **52** 291 (1999).
[22] I.S. Tashlykov, W. Wesch and E. Wendler, paper presented at III International Symposium, New Electrical and Electronic Technologies and their Industrial Implementation, Lublin, Poland, 13–16 May (2003).