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# Composition of Co films/Si substrate systems prepared by means of self-ion assisted deposition and accompanying silicon damage

**Abstract.** The composition, radiation damage and morphology of silicon modified by means of self – ion assisted Co deposition was investigated.

**Streszczenie.** Zbadano skład i uszkodzenia radiacyjne krzemu zmodyfikowanego podczas naniesienia powłok Co metodą dynamicznego mieszania jonowego. (**Skład i uszkodzenia radiacyjne krzemu w strukturach warstwa Co – podłoże krzemowe wytwarzanych w warunkach dynamicznego mieszania jonowego**).

**Keywords:** Co/Si structures, composition, damage, topography.
**Słowa kluczowe:** struktury Co/Si, skład, uszkodzenia, topografia.

## Introduction

Coatings of materials are widely used for scientific and technical challenge that is crucial for functional, protective or decorative layers. Among the various vacuum methods employed, 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 used for ion assistance 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 is used. Inevitably this a source will also produce contaminant species. For example, metal ($Cr$, $Zr$, $Mo$) layers deposited on substrate by means of self-ion assisted deposition (SIAD) at 5 — 20 keV consist of metal, carbon, oxygen, hydrogen derived from the residual vacuum and vacuum oil [8-10]. These films are of scientific interest and practical significance. They have controlled adhesion between the substrate and the film and offer a substantial reduction in friction force against a rotating steel shaft and a sliding steel pin under non-lubricated conditions when, for example, rubber is a substrate [9]. Deposition of metal-based films changes wettability of the modified rubber surface [11]. As well as the composition of coating, the hydrogen in the coating, at the coating – substrate interface is 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 cobalt films on silicon. Additionally the accompanying damage of silicon structure during ion assisted deposition of thin $Co$ films is discussed.

## Experimental section

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 a resonance vacuum arc source (RVAS) with cobalt electrodes to produce a mixture of $Co$ atoms and $Co^+$ ions attached is. Substrate (silicon wafers) was floated to a negative potential with respect to the source of 7 kV to accelerate the ion species. The SIAD system was pumped by a conventional diffusion pump and attained during film deposition a base pressure of $10^{-2}$ Pa.

The relative ratios of ions ($I$) to neutrals ($A$) could be changed by varying the parameters of the RVAS and $I/A$ was between 0.1 and 0.3. Measured film deposition rates were between 0.2 and 1.2 nm/min. Note that the film growth rates were so low in this experiment because of the role of self sputtering which is a significant factor of the ion energy used. To investigate atom mixing processes at an interface region of a coating/substrate it is useful to know a position of initial surface of substrate (PISS). For this purpose we implanted $Xe^+$ ions in the part of substrates. The energy of ions was 10 or 40 keV, doses — in range $1 \cdot 10^{14} – 2.7 \cdot 10^{15}$ $Xe$/cm$^2$.

The composition of the coating/substrate structures and the damage of substrate irradiated with $Xe^+$ ions, or $Co^+$ ions, or $Xe^+$ and $Co$ together were investigated using Rutherford Backscattering/Channeling Spectroscopy. The energy of the $He^+$ ions was 2.0 MeV and the energy resolution of analyzing system was 25 keV. The experimental RBS data for concentration against depth were compared with data from the RUMP code simulation [12]. The damage profiles were constructed using the known technique [13].

The $H$ concentration 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 [14]. The procedure employed for the $H$ profiling has been described elsewhere [15].

Roughness parameters of virgin silicon substrate and substrate with $Co$ coatings were measured using atomic force microscope NT-206 and corresponding software.

## Results and discussion

Damage depth distribution in substrate as well as composition information of the coatings deposited on $Si$ with inserted $Xe$ marker at a mean rate of 1.1 nm/min during 2 hours under self–ion bombardment by $Co^+$ ions at 7 keV were evaluated using RBS/Channeling spectra. RBS analysis of film composition (shown in Fig.1) indicates that the deposited thin layer has a multi-component structure.

It is estimated that the $Co$ deposition using the SIAD process is accompanied by appearance of carbon, oxygen, silicon in the coating. 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 by a RUMP simulation for all other measured component peak intensities. A complete concentration – depth profile for a sample having $Co$, carbon, oxygen, silicon and hydrogen has been obtained from the original spectra using a standard computer program [12] and predicts that the $Co$–based film thickness is 140 – 150 nm. Fig.2 indicates that the $Co$ concentration decreases from the top surface of the coating to a value about 60% lower near the PISS.
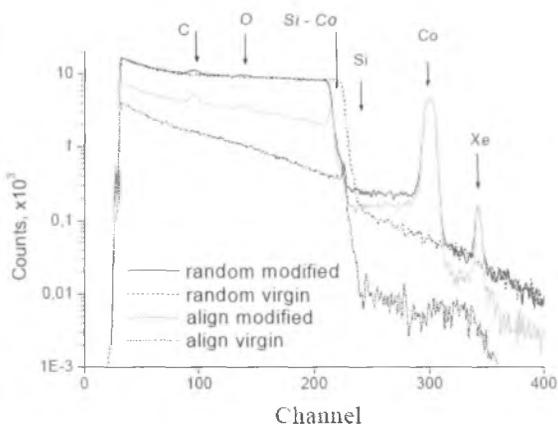
Fig. 1. Energy spectra of backscattered He ions with $E_o$=2.0 MeV from virgin (100) $Si$ and $Co/Si$ structure obtained using SIAD and $Xe$ ion implantation, $E_{xe}$ = 10 keV, $D$ = 1×10$^{14}$ cm$^{-2}$



Fig. 2. Relative content of species in SIAD Co thin film on silicon: a – only SIAD process; b – SIAD process after $Xe$ ion implantation (PISS – position of initial surface of substrate)

The cobalt "tail" in silicon as seen in Fig.2 $a$ indicates that $Co$ atoms penetrate deep into silicon during SIAD process, probably, because of the influence of high energy density deposited into collision cascades [5,16]. The hydrogen level in coating follows an exactly similar trend, which suggests that there is at least some combination of hydrogen with $Co$ to form a hydride. The carbon and oxygen levels show an increase near the coating/$Si$ interface. The high $O$, $C$ and $H$ content arises, we suppose, because of the vacuum conditions used, and it allows deposition of oxyhydrocarbons onto the growing film and accumulation of them during irradiation by the accelerated $Co^+$ ions. We may consider the films created by SIAD as films whose composition may be compared with that of solid lubricant films [17].

It is also clear from the RBS data that there is a significant out diffusion of $Si$ from substrate into the coatings, stimulated by the self – ion irradiation. The $Si$ content falls slightly toward the surface. A driving force for the significant out diffusion of $Si$ atoms into the coating is, probably, the same as for penetration of $Co$ atoms into silicon, namely the high energy density deposited in the collision cascade. In such circumstances a shock wave created in the thin film/substrate system during relaxation of thermal spikes can promote inter- and out-diffusion of coating/substrate species [18].

It is observed that implantation of $Xe^+$ ions influences significantly on the depth distribution of the coating components in substrate, Fig. 2 $a, b$. It means that additionally to the high energy density deposited in the collision cascade radiation defects generated in substrate by $Xe^+$ ions increase diffusion processes in the thin film/substrate construction.

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. The experimental results confirm the RBS – RUMP data about the huge amount of hydrogen in the $Co$-based coatings prepared by means of SIAD [19]. This result is in agreement with Vistrom et al [20], where it was shown that evaporated films of a variety of metals may contain concentrations of $H$ many orders of magnitude greater than the bulk solubility. The high concentration of $^1H$ in $Co$–based films may serve as evidence that the films contain large concentrations of $^1H$ traps. The traps may be associated with grain boundaries, they may also be voids. It is known [21] that the difference in the behavior 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 Fig. 3, the damage profiles observed after $Co$ coating deposition on virgin wafer (100) $Si$ and previously implanted are demonstrated.



Fig. 3. Experimental damage profiles in (100) $Si$: 1 – implanted with $Xe$ ions, $E_{xe}$ = 40 keV, $D$=9×10$^{14}$ cm$^{-2}$; 2 – with SIAD $Co$ thin film, $E_{Co}$ ≈ 7 keV;, 3 – after SIAD $Co$ thin film on previously $Xe$ ion implanted substrate

The defects in silicon near thin film and $Si$ substrate interface are generated by irradiation of (100) $Si$ wafer with $Co^+$ ions at the initial stage of the coating deposition. When $Co$ coating is deposited on previously implanted with $Xe$ ions part of $Si$ wafer we observed decreasing of the defect concentration in maximum of $Xe$ generated damage profile and broadening of the profile in general, Fig. 3. That means the defects — interstitial $Si$ atoms, diffuse in depth of the substrate and to the PISS and further in coating. In this case even some annealing takes place. For example, in Fig. 4 curves 2 are under curves 1 for both 10 and 40 keV energies of $Xe^+$ ions.

One of the most noticeable results of coating deposition on solid surface is modification of its roughness. Therefore we investigated changes of $Si$ surface roughness after deposition of $Co$ coatings. Selected example of surface topography of $Co$/substrate structure is shown in Fig. 5.
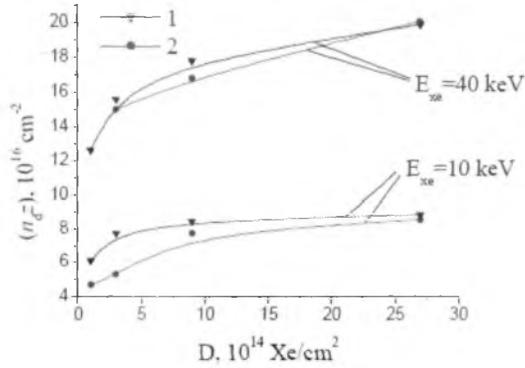


Fig. 4. Layer defect concentration in (100) $Si$ in dependence on $Xe$ ion doses: 1 – only $Xe$ ion implantation, 2 – $Xe$ ion implantation and SIAD of $Co$ thin films
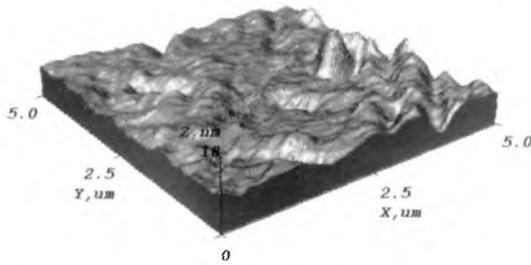


Fig. 5. Three-dimensional AFM surface morphology of silicon with SIAD $Co$ coating

Results of AFM measurements of virgin and modified $Si$ nanoroughness parameter are presented in Table 1.

Table 1. Changes of vertical roughness parameters of $Si$ after SIAD of $Co$ thin film

| Parameter, | Virgin $Si$ | $Si$ with $Co$ coating |
|---|---|---|
| Rave, nm | 0,169 | 0,744 |
| (Surface area)/(Projected area) | 1,0027 | 1,0073 |

Generally, the changes of the roughness parameters are within nanometer range in our case. That is why it can be concluded that SIAD process of $Co$ thin films on silicon is appropriated for microelectronics.

## Conclusion

We have shown that $Co$ coatings produced by means of SIAD have a multi-component structure. Thin films deposited on silicon consist of $Co$, $C$, $O$, $Si$ and $H$. The high content of $C$, $O$ and $H$ arises, we suppose, because of the poor vacuum used, and it allows capture of oxyhydrocarbons onto the growing film and accumulation of them under irradiation with the accelerated $Co^+$ ions. Silicon appears in the coatings due to an out-diffusion process from the bulk. Deep penetration of $Co$ atoms into silicon and appearance of $Si$ atoms in coatings are attributed to radiation-enhanced diffusion processes during self-ion assisted deposition of thin cobalt-based films upon silicon. Implantation of $Xe^+$ ions in substrate before deposition of $Co$ coatings promotes radiation-enhanced diffusion of components in $Co$/$Si$ structures.

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

The changes of all roughness parameters examined by AFM and relating to vertical features of virgin and modified by $Co$ coating deposition $Si$ surfaces testify high quality of $Co$ coating/$Si$ substrate structure that shows that Self-Ion Assisted Deposition process of $Co$ coatings on silicon may be applied in microelectronics.

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