DESIGN AND INVESTIGATION OF CORROSION RESISTIVE SIC-RICH NANOLAYERS

THESES

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1. Introduction and Aims

In our days, almost all functional materials from the display of smart phones, through instruments till the engines of rockets are protected against environmental effects. Protective layers have been used already in Ancient Egypt when people used tar and balsam for plugging ships. The need for these layers had been increased due to industrial revolution and mechanization, just think about anticorrosive coatings from which enamel was preferred the most. In the meantime the development of technologies led to the production of thin films. These are such micro and nanomaterials which are made on the surface of solid substrates, their thickness is between atomic sizes and some 100 micrometers. These thin films might have several advantageous properties such wear-, heat-, and corrosion-resistance and high hardness. They are also applied in micro and nanoelectromechanical (MEMS/NEMS) systems as it important to secure long-term operation for sensors. For producing protective layers often high temperature and high pressure processes are needed. In many cases the substrate can not tolerate such conditions e.g.: MEMS/NEMS; the stable material can be produced by far from equilibrium conditions method. Among others, ion irradiation is a method which is able to produce materials at room temperature for which generally high temperatures are needed. If we irradiate a layer structure at the interfaces atomic mixing, or ion mixing happens. The ion-mixed layer is far from thermodynamic equilibrium, therefore chemical reaction can happen below the routine temperature. By means of ion bombardment we can influence the width of boundary layer transition and the solid phases forming there. The method has been applied from the 1980s for producing thin layers of metastable compounds which have advantageous properties. Formerly, for these purposes high energy (MeV) ions were applied; the layers produced were some ten nanometer thick and located some ten nanometer far from the surface.¹ Decreasing the ion energy, thinner – some nanometers thick - layers can be created which are located close to the surface. In our laboratory there is a great experience in investigating the mixing of several multilayer – Si-Ge², Ni-C³, Cr-Si⁴, Ta-C⁵, Si-C⁶ -

Recently in our laboratory we have succeeded to produce silicon-carbide (SiC) at room temperature, applying focused ion beam method (FIB) by irradiating C/Si (10-20 nm) multilayer structures with gallium (Ga) ions. SiC is a material with many advantageous properties such biocompatibility, high heat resistance, high wear resistance, good thermal conductivity and high corrosion resistance. Among others it is used as a protective layer in MEMS/NEMS systems, which are operating in harsh environments e.g. automotive and aerospace applications such as combustion processes or gas turbine controls. As it protects from chemicals and heat better than silicon does it is capable to protect Si-based sensors. The disadvantages of the Ga irradiation applied in our laboratory for producing SiC was a. the accumulated high Ga concentration b. it is quite costly and is not feasible for irradiating macroscopic areas. Thus the Ga irradiation is not appropriate for production of protective layers. Therefore the laboratory switched to noble gas irradiation which is scalable up to wafer size. Corrosion studies on the layers produced have not been performed, however.

My aim is to investigate the corrosion properties of the ion beam-mixed layers. First I deal with the production of the layer, I investigate the dependence of the formation of SiC from the parameters of the nobles gas irradiation. Therefore I change the projectile, the fluence, the energy of the mixing ion and the layer structure. I characterize the chemical resistance of the variously produced layers by means of potentiodynamic measurements.

corrosion test. I hope to establish a correlation between the irradiation parameters and the chemical resistance.

There are various simulation techniques for modelling the ion bombardment. These are continuously developing to provide more and more precise results within the range of wide irradiation parameters. By these methods the modelling of ion mixing is limited due to the high-computation-intensity. Therefore we used simulations applying simpler descriptions with many assumptions which are faster. Such simulations are: SRIM and TRIDYN. Therefore it is interesting to investigate whether it is possible by such simulation techniques with limited validity to predict the corrosion properties of our layers, hence this would facilitate and speed up the design of the protective layer.

Another interesting area is producing SiC patterns. Applying ion irradiation through masking layer it is possible to produce SiC patterns in one step. In this case the compound formation and the creation of patterns take place simultaneously at room temperature; this would facilitate the standard procedures.

2. Experimental methods

The irradiated three different C/Si multilayer systems were produced by magnetron sputtering in the Jozef Stefan Institute, Ljubljana. The systems differed in the thickness (10-20 nm) and the order of layers. The layers were irradiated by argon and xenon ions. In the case of argon ions the applied energy was 40 keV, the fluence \(0.25 \times 10^{16} \text{ Ar}^+/\text{cm}^2\), in the case of xenon ions the energy was 120 keV, the fluence \(0.25-3 \times 10^{16} \text{ Xe}^+/\text{cm}^2\). The SiC formed due to irradiation was identified by Auger electron spectroscopy (AES). For determining the in-depth distributions of the components AES depth profiling using argon ions was applied. For investigating the chemical resistance of the mixed layer I performed potentiodynamic corrosion test in 4M KOH solution, in a three-electrode cell. From the measured Tafel curves I determined the corrosion rates of the sample. For predicting the effects of irradiation I applied TRIDYN simulation. For each irradiation I performed the simulation and calculated the SiC in-depth distribution. For creating the nanostructures I applied two different masking layers, one was a Langmuir-Blodgett film made from silica particles (diameter 590 nm), the other one a


SRIM Stopping and range of ions in matter by Ziegler, J. F. version SRIM, 2013 Software freely available www.srim.org

grid of a periodicity of 2 µm. After the irradiation (120 keV, $3 \times 10^{16} \text{Xe}^+/\text{cm}^2$) and mask removal the formed SiC was identified by AES depth profiling. The non-irradiated part was removed by etching in microwave plasma and in HF/HNO$_3$ solution which led to 3D structure formation. The pattern morphology was investigated by atomic force and scanning electron microscopy.

3. Results

3.1. Production of corrosion resistant layer by means of ion beam mixing

The performed AES depth profiling on the irradiated samples has shown that the in-depth distribution of SiC can be tuned by changing the irradiation parameters (fluence, energy) and the layer structure. Fig. 1 shows, as an example, the effect of a $6 \times 10^{16} \text{Ar}^+/\text{cm}^2$, 40 keV irradiation on the sample with a structure of C (20 nm) / Si (20 nm) / C (20 nm) / Si (20 nm) / C (20 nm) / Si substrate. Fig. 1a presents the AES depth profile of the non-irradiated sample, while Fig. 2a shows the profile of the irradiated one. We can see that the in-depth distribution of the non-irradiated sample exhibits C and Si layers with sharp interfaces and the individual thicknesses are the same. Fig. 1b shows that due to the irradiation serious changes occurred in the sample; namely, an intermixing took place. The first Si layer (below the topmost C layer) practically disappeared; it was consumed by the SiC production. On the other hand, only a part of the second Si layer was converted to SiC. This can be understood considering the projected range of the 40 keV Ar$^+$ being about 40 nm for this sample. The last carbon layer remained more or less untouched. Considering the shape of the SiC distribution e.g at 60 and 70 nm one can conclude that the SiC is growing from the interfaces.

![Fig. 1. AES depth profiles of the 20-20 sample (a) pristine and (b) irradiated ($6 \times 10^{16}$ Ar$^+/\text{cm}^2$, 40keV)](image-url)
In Fig. 1 we could see that a high amount of carbon remained unreacted. This is due to the atomic density of C (112.8 atoms/nm$^2$) being two times more than that of Si (49.9 atoms/nm$^2$), therefore the carbon layer contains two times more atoms. Consequently, for this sample structure, even if all the Si is converted to SiC, still half of the C remains unreacted. If we want to have an intermixed layer without the presence of C, evidently its layer thickness should be decreased. Fig. 2 shows the results of the irradiations for these layer structures. The argon projected range for these structures is 42 nm, the xenon is 57 nm. We can see that various SiC distributions can be produced by varying the fluence: applying 120 keV, 3 × 10$^{16}$ Xe$^+$/cm$^2$ irradiation a quasi continuous distribution of SiC can be achieved.
if the SiC concentration is lower than 20% then the layer cannot resist to the chemical attack. Moreover, the distributions are not continuous except in case of the high fluence Xe\(^+\) irradiation. To account for these facts we define the effective areal density as follows: the integral of SiC from that depth where its amount is higher than 20% until that depth where its concentration goes below 20% again. Fig. 3 shows the corrosion rate vs. effective areal density for all measured data obtained from all layer structures which were irradiated by various ions, energies and fluences. It can be seen that they are in good correlation even though the SiC distributions are strongly different. This means that I could find a correlation between effective areal density of the SiC produced by ion mixing and the chemical resistance.

![Graph](image)

**Fig. 3.** Corrosion rates vs effective areal density of SiC for the variously irradiated different layer structures, the fitted curve serves only for leading the eyes

### 3.2. Describing the effects of ion irradiations by means of simulation techniques

If one wishes to tailor the corrosion resistance of a given sample; with the help of Fig. 3 one must determine and produce the SiC amount and distribution necessary to reach the desired corrosion resistance. Using an experimental approach is rather time consuming and expensive, however. To address the problem we have looked for other possible solutions. To address the problem we have looked for describing the mixing process in a theoretical way. For these purposes I applied TRIDYN simulation. We
have frequently applied this simulation which either well\textsuperscript{15} or poorly\textsuperscript{3} described the mixing process of layer structures. In the case of the Si-C system we have shown that the TRIDYN simulation provides good prediction of the SiC distribution that evolves due to IBM.\textsuperscript{14}

Calculating the depth profiles of all irradiations and extracting the effective areal densities of SiC and plotting them as a function of the measured corrosion rates we get a curve similar to that we get in the case of Auger spectra. (Fig. 4.) This clearly shows that by applying fast and cheap simulation techniques the design of corrosion resistive layers is possible and the expensive experiments can be set off.

![Fig. 4. Corrosion rates vs effective areal density of SiC calculated from TRIDYN for the variously irradiated different layer structures, inset enlarged y axis, the fitted curve serves only for leading the eyes](image)

**3.3. Formation of patterns**

We can say that the creation of SiC patterns and afterwards the 3D structures at room temperature was successful. Due to irradiation the compound formation and patterning happened in one step. AES depth profiling proved that in the irradiated region - non-protected by mask - a SiC-rich region formed.

For better understanding the process of producing 3D structures is depicted in Fig. 5a. The AFM images of the 3D structures created by the help of LB film and litographic grid can be seen in Figs. 5b and c. We can see that by varying the applied masks and etching procedures (etching HF/HNO₃, microwave plasma) various 3D structures can be achieved.

**Fig.5.** a. Process of producing 3D structures b. AFM image of the LB-masked sample after mask removal and one step HF/HNO₃ etching and one step oxidation. c. AFM image the grid-masked sample after mask removal and HF/HNO₃ etching, oxidation and additional HF/HNO₃ etching.
4. Theses

T1. I demonstrated that by irradiating C/Si nanolayer structures of different thicknesses, layer numbers and orders built on a Si wafer with Ar⁺/Xe⁺ ion the in-depth distribution of the forming SiC can be tuned by changing the parameters and the layer structure. [S1, S2]

T2. I showed that the corrosion rate of the sample subjected to the lowest fluence is order of magnitudes lower than that of pure silicon. I demonstrated that the corrosion resistance of the mixed layer does not depend on the whole amount of the formed SiC. However, I could introduce the effective areal density of SiC which is in good correlation with the corrosion rate of the mixed layers. [S2]

T3. I demonstrated that by selecting the relocation threshold energy properly the TRIDYN simulation describes the mixing process well. I managed to create a simple rule which describes the SiC formation in the mixed layer. Hence, the TRIDYN simulation is suitable for calculating the effective areal density of SiC, therefore the design of corrosion resistive protective layers is possible for a wide range of layer structures, ions, ion energies and fluences. [S3]

T4. I elaborated a method for creating nano-sized SiC patterns which consists of SiC and Si or C surfaces. I showed that mounting a mask on a Si/C layer structure the ion irradiation creates SiC patterns at room temperature, hence the compound and pattern formation happens in one step. This 2D structure can be transformed by applying various etching procedures (etching HF/HNO₃, microwave plasma) into various 3D structures. In the 3D structure SiC is in the original surface and the holes are Si or C bottoms where the diameter and the depth of the hole can be tuned by the dimensions of the applied layer structure and mask [S4].

5. Application possibility

I hope that our method developed for producing SiC protective layers will be used for protecting MEMS/NEMS systems. In the future it would be worthy to check whether it is possible to produce other potentially protective layers at room temperature by means of ion beam mixing.
6. Publications

6.1. Publications related to the theses


6.2. Presentations


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