INTERACTION OF HYDROGEN PLASMA WITH CORRODED SILVER SURFACE

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Key words: materials for electrical contacts, cleaning of contacts, surface cleaning, cleaning of contact surfaces, cleaning of metals, plasma cleaning, discharge cleaning, electrical discharges, H-plasma, hydrogen plasma, archeological artifacts, H-plasma interaction with surface, corroded surfaces, material corrosion, surface corrosion

Abstract: Experimental investigation on discharge cleaning of corroded silver surface has been performed. Samples of silver with a thin and thick corroded layer were used. In the case of a thin layer, the surface of pure silver was contaminated with fingerprints. AES analysis showed that the layer with the thickness of 20 nm consisting of O, S, Cl and C was formed. In the case of a thick layer, a well corroded silver coin from 19th century was used. In this case, the thickness of the corroded layer was of the order of 0.1 mm and the EMPA investigation showed it was an agglomerate consisting of O, S, Cl, Si, C, Fe, Ti. All samples were exposed to a low pressure weakly ionized hydrogen plasma at the pressure of 1 mbar. Plasma parameters were measured with a double Langmuir probe and a catalytic probe. The electron temperature was 6eV, plasma density $2.10^{16}m^{-3}$, and the degree of dissociation of hydrogen moleculs about 1%. Samples with the thin corroded layer were exposed to plasma for 10 minutes. AES analysis of the treated samples showed that all impurities were completely removed from the surface. The coin was exposed to hydrogen plasma at the same conditions, and the EMPA analysis showed that concentration of oxidizing impurities was lowered but other impurities still persisted.They could not be removed solely by treatments in plasma, but successive treatment in plasma and ultrasound bath. By the combination of both treatment we were able to decrease the concentration of any impurities below the detection limit of the EMPA.

Interakcija vodikove plazme s korodirano površino srebra

Ključne besede: materiali kontaktov električnih, čiščenje kontaktov, čiščenje površin, čiščenje površin kontaktov, čiščenje kovin, čiščenje plazemsko, čiščenje razelektritveno, razelektritve električne, H-plazma vodikova, artefakti arheološki, interakcija H-plazme vodikove s površino, površine korodirane, korozija materialov, korozija površin

Povzetek: Prikazujemo rezultate eksperimentalne preiskave plazemskega čiščenja korodirane površine srebra. Uporabili smo srebrne vzorce s tanko in debelo korodirano plastjo. V primeru tanke korodirane plasti smo površino čistega srebra kontaminirali s prstnimi odtisi. AES preiskava teh vzorcev je pokazala, da je na površini prisotna tanka plast nečistoč debeline 20 nm, ki vsebuje poleg srebra še O, S, Cl in C. V primeru debele plasti smo izbrali močno korodiran srebrni kovanec iz 19. stoletja. V tem primeru je bila debelina korodirane plasti reda velikosti 0,1 mm. Preiskava vzorca z elektronskim mikroanalizatorjem je pokazala, da površinski aglomerat vsebuje naslednje elemente: O,S,Cl,Si,C,Fe in Ti.

Vsi vzorci so bili izpostavljeni nizkotlačni šibkoionizirani vodikovi plazmi pri tlaku 1mbar. Plazemske parametre smo merili z dvojno Langmuirjevo sondo in katalitično sondo. Elektronska temperatura je bila 6 eV, gostota plazme $2x10^{16}$ m^{-3} in stopnja disociiranosti vodikovih molekul okoli 1%. Vzorci s tanko korodirano plastjo so bili izpostavljeni vodikovi plazmi za 10 minut. AES preiskava tako obdelanih vzorcev je pokazala, da smo odstranili vse nečistoče površin. Kovanec je bil izpostavljen vodikovi plazmi pri enakih pogojih in analiza z elektronskim mimkroanalizatorjem je pokazala, da je po obdelavi koncentracija oksidativnih nečistoč bistveno zmanjšana, medtem ko so ostale nečistoče na površini še vedno prisotne. Slednje nismo uspeli odstraniti samo z plazemskim čiščenjem temveč smo jih uspešno odstranili s kombinacijo plazemskega in ultrazvočnega čiščenja. S kombinacijo obeh metod smo uspeli kovanec tako dobro očistiti, da je koncentracija katerih koli nečistoč na površini manjša kot je meja detekcije elektronskega mikroanalizatorja.

1 Introduction

Discharge cleaning has become a widely used method for removing surface impurities. Active particles which are created in plasma, interact with surface impurities forming volatile molecules which are easily desorbed and pumped away. By creating plasma in a mixture of various gases, it is possible to remove different types of impurities. For reduction of surface layers of oxides, hydrogen or a mixture of a noble gas and hydrogen is usually used. In the past decade, this method has been widely investigated as it is of a great scientific and commercial importance. The method has been successfully applied in cleaning of stainless steal surfaces of tokamaks /1,2,3/, silicon in microelectronic devices /4,5,6,7/ and a variety of metals and alloys archaeological artifacts are made from /8,9,10/. Although hydrogen plasma can be created by different DC and high frequency discharges, the radio frequency (RF) and microwave (MW) discharges are the most suitable for this application. This is due to the fact that a plasma with a smal space potential can be created with a high frequency discharge, and it penetrates fairly well in gaps between samples. The degree of ionization in a high frequency discahrge is usually low (between 10^{-6} and 10^{-2}) /11,12/, except in the case the electron cyclotrone resonance (ECR) conditions are met /13/. In the latter case, the degree of ionization can be more than 10% /14/. In any case, the degree of dissociation of hydrogen molecules is more than 1% /12/ and can approach unity if a plasma is created in a discharge vessel made of material with a low recombination coefficient for the reaction $2H \rightarrow H_2$, i.e. different glasses, alumina, some ceramics /14/.

Despite the discharge cleaning of silver and its alloys is of a great importance in electronic industry as it is an excellent method of final treatment of contact materials, little work on this subject has been published. In the present paper, we describe experimental work recently done at our laboratories on discharge cleaning of silver with a thin and a thick layer of impurities.

2 Experimental

Experiments were carried out in a vacuum system, which consisted of a discharge vessel, a liquid nitrogen cooled trap and a two stage mechanical rotary pump.

The base pressure in the system was 10^{-3} mbar. The discharge vessel was a glass cylindrical tube with the lenght of 80 cm and the diameter of 4 cm. Plasma in the discharge vessel was created at the pressure of 0.5 mbar by an inductively coupled RF generator with the frequency of 27.12 MHz and the maximum output power of 700 W. Plasma parameters were measured with a double Langmuir probe /15/, and a catalytic probe /14,16/. The electron temperature in plasma was 6eV, while the plasma density was 2.10^{16} m^{-3}.

The use of a liquid nitogen cooled trap was found to be very important not only as a trap for oil form the rotary pump, but especially as a trap for aggresive gases forming during the discharge treatment of well corroded samples. Namely, during the treatment of archeological artifacts, a rather large amounts of H_2S and HCl were produced, and both of the gases could have been harmful to the pump.

Two types of samples were prepared: i) strips made of pure silver, and ii) old silver coins. The strips were first cleaned with freon and than touched well with fingers in order to obtain a thin layer of different impurities on the surface. The coins were discovered recently, and only the layer of sand and soil was removed by an archeologist. We treated them in ultrasound bath in a mixture of water and detergent in order to remove weakly bonded impurities from the samples, mostly hydrocarbonaceus compounds.

Samples with a thin layer of surface impurities were analyzed with an Auger electron spectroscopy (AES) depth profiling. We used a scanning Auger microprobe (Physical Electronics Ind. SAM 545 A) with a static primary electron beam with the energy of 5 keV, the beam current of 0.5 μA, and the beam diameter of about 10 μm. The incidence angle of the electron beam with respect to the normal of the surface plain was 30°. In order to obtain depth profile, samples were sputtered with Ar^+ ions with the energy of 1keV, rastered on a surface area larger than 10 x 10 mm^2. Atomic concentrations were calculated by taking into account relative sensitivity factors according to the literature /17/. The concentrations are plotted against ion gun sputter time instead of the depth, and 1 minute sputter time corresponds to the depth of about 2 nm.

The thickness of the layer of impurities on silver coins was too large to be analyzed with AES depth profiling, and the method is destructive anyway. The concentration of elements on the surface of these samples was determined with an electron microprobe analysis (EMPA). A scanning electron microscope JEOL JSM 35 with an energy dispersive X ray microanalyser (EDX-TRACOR TN 2000) was used to determine the concentration of elements in the surface layer. An electron beam with the voltage of 20 kV and current of approx. 0.5 mA was focused at the sample in a spot of about 1 x 1 μm^2. The thickness of the layer analyzed by EDX was about 1 μm.

3 Results

The composition of the surface layer of industrial cleaned silver strips and those contaminated with fingerprints was analyzed with AES depth profiling and is shown in Figure 1 and 2, respectively. It is noticeable that both samples contain a surface layer of impurities with the thickness of the order 0.1 μm . The composition of the impurity film on the samples is only slightly different. Both samples contain mostly carbon (probably an organic compound), oxygen, chlorine, sulphur and potassium.

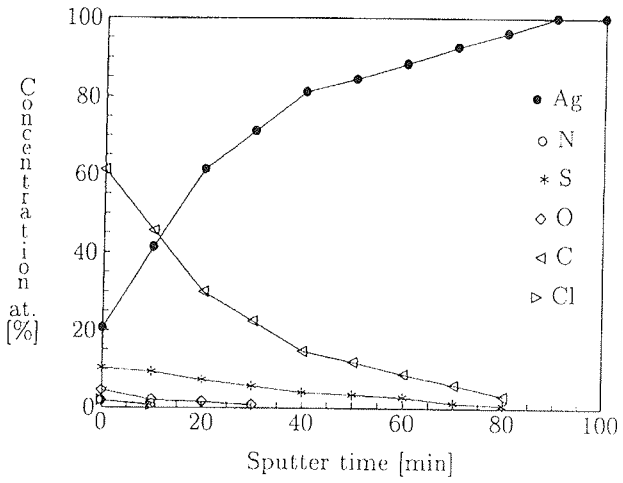

Fig. 1. AES depth profile of the surface layer of the industrial cleaned silver strip.

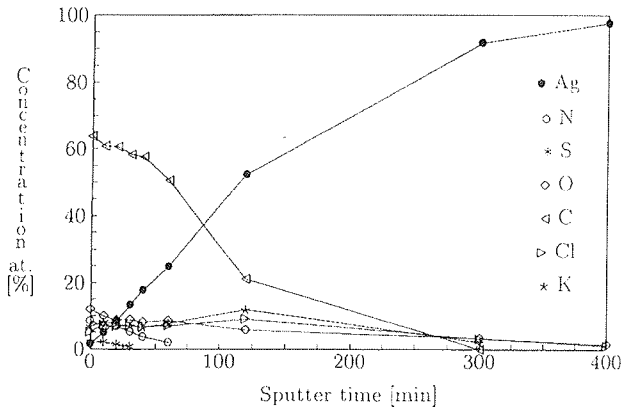

Fig. 2. AES depth profile of the surface layer of the silver strip cleaned with freon and later contaminated with finger prints.

Both samples were mounted in the middle of the discharge vessel and treated with hydrogen plasma for 10 minutes. Due to the recombination of atomic hydrogen on the sample surfaces, the absorption of UV light from plasma, and the bombardment of the surfaces with charged particles, the temperature of the samples raised to about 150°C. After the treatment the samples were exposed to air for a short time and analyzed with AES sputter depth profiling again. The composition of the surface of the samples is shown in Figure 3 and 4. It is noticeable that the surface of both samples is clean except of traces of oxygen and sulphur which were probably adsorbed on the surface during the exposure of the samples to air.

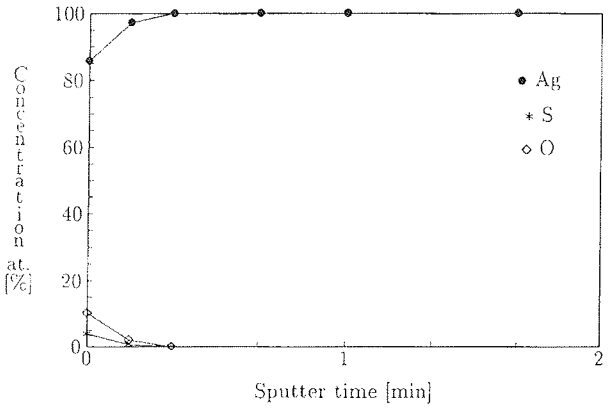

Fig. 3. AES depth profile of the surface layer of an industrial cleaned silver strip which was exposed to hydrogen plasma for 10 minutes.

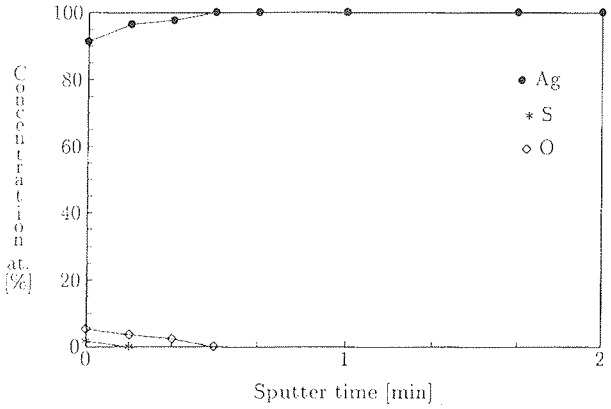

Fig. 4. AES depth profile of the surface layer of a silver strip first cleaned with freon, than contaminated with finger prints and exposed to hydrogen plasma for 10 minutes.

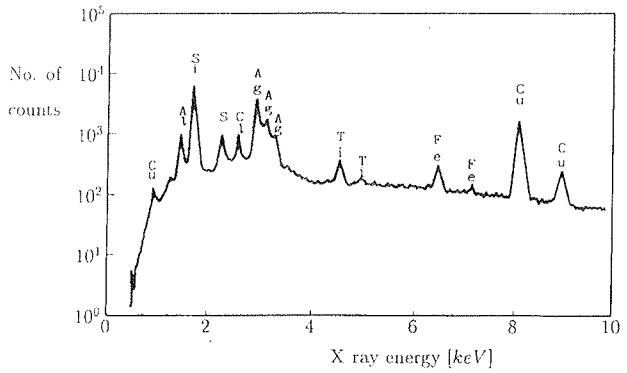

Fig. 5. EDX spectrum of the surface layer of the silver coin before discharge cleaning.

Before the plasma treatment, a silver coin was analyzed with EMPA (Figure 5). Apart from oxygen and carbon, which cannot be detected with our microprobe, the layer of impurities of the surface consisted of silver, iron, copper, silicon, sulfur, and chlorine.

The sample was treated with plasma for 10 minutes. After the treatment it was analyzed with the electron microprobe. The only change was a substantial enlargement of iron peak. It was also found that, after the plasma treatment, the layer of impurities on the surface can be rather easily removed mechanically by the use of a needle. Since we did not want to make any scratch on the sample, we rather treated it in the ultrasound bath and some impurities were released. Microprobe analyses showed that the concentration of iron fell to the original value. The sample was then treated again with plasma for 10 minutes. After this treatment, a part of the surface became clean, while most of the surface was still covered with a layer of impurities. The microprobe analyses showed that the clean part of the surface consisted of silver and about 10% of copper (which is actually the structure of the bulk), and the dirty part of the surface consisted of iron, silver, copper, sulfur and chlorine. After repeating the plasma cleaning and the ultrasound cleaning for four times, all the surface became clean. The microprobe analyses showed only silver and cooper, while the concentration of other elements was below the detection limit of the microprobe which was about 01. at.% (Figure 6).

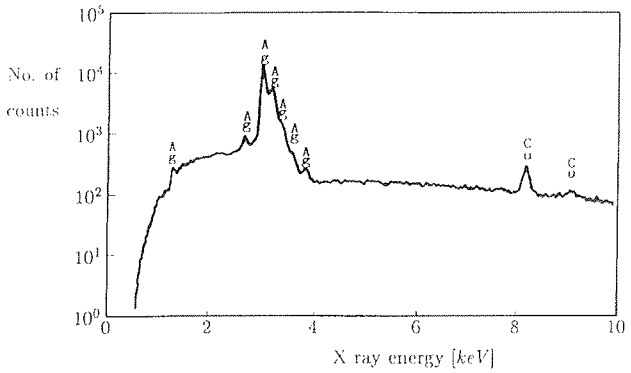

Fig. 6. EDX spectrum of the surface layer of a silver coin after successful cleaning in hydrogen plasma and ultrasound bath.

4. Discussion

The experiments described above showed that active particles produced in hydrogen plasma react with the impurities bonded to the surface of the samples. Since the density of plasma is low it is obvious that hydrogen ions do not contribute much to the cleaning efficiency. It is probably atomic hydrogen which reacts with the surface impurities. Hydrogen atoms react with chemically bonded oxygen, chlorine, and sulfur to form molecules, which are easily pumped from the discharge vessel: OH, H_2O, HCl, H_2S, etc. These gases are then trapped by the liquid nitrogen cooled trap.

The appearance of iron in the impurity layer after the plasma treatment can not be due to a deposition of iron since plasma was not in a contact to any material composed of iron. A small amount of iron was presented within the layer of impurities already before the

treatment. The original concentration of iron is rather low. During the discharge treatment, most of other impurities were removed from the surface, so the relative concentration of the iron in the surface layer was increased substantially.

Iron cannot be removed from the surface with mild hydrogen plasma cleaning. Further-more, a layer of iron on the surface probably causes intensive recombination of atomic hydrogen on the surface and thus prevents successful removal of other impurities from deeper layers. Luckily, the layer of iron is weakly bonded to the surface, so it can be successfully removed mechanically either by the use of a needle or even by the use of ultrasound treatment. Once the layer of iron is removed, further removal of other impurities in hydrogen plasma can take place, so that after repeating the discharge cleaning and the ultrasound cleaning for several times, the surface of the samples became free of any impurities.

5. Conclusion

Discharge cleaning experiments on silver samples were carried out in low pressure weakly ionized hydrogen plasma. It was shown that most impurities can be removed from the samples by treatment in hydrogen plasma with the density of 2.10^{16} m^{-3} and the electron temperature of 6 eV. In the case of a thin layer of impurities, the samples were analyzed with AES depth profiling and it was shown that a layer of chemically bonded oxygen, chlorine, sulfur, carbon and silicon can be completely removed in ten minutes. Discharge cleaning of well corroded silver coins took nearly an hour. In this case, it was shown that iron, which was also presented in the layer of impurities, could not be removed by treatment in hydrogen plasma. Furthermore, it prevented sucessful removal of other impurities. A successful procedure of removal iron from the surface was found to be the ultrasound tretament. By repeating the discharge and ultrasound cleaning procedures it was possible to remove a thick layer of impurities as well.

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