

ANALYSIS OF CONTACT LAYERS IN MINIATURE ELECTRICAL RELAYS WITH AUGER ELECTRON SPECTROSCOPY

L.Koller, B.Praček, S.Vrhovec, D.Railič

Institut za elektroniko in vakuumsko tehniko, Ljubljana, Slovenija

Keywords: electrical contacts, miniature relays, contact quality, cleaning of contacts surfaces, ion etching, sputter-etching processes, AES analysis, AES, Auger electron spectroscopy, surface composition of contacts, contact surface contamination, contact alloys, impurities of alloys, impurity detection

Abstract: The surface composition of miniature electrical relay contacts was investigated with Auger electron spectroscopy. Surprisingly, large amounts of contaminants (carbon, sulphur, oxygen, calcium), were detected in addition to gold, iron, nickel and cobalt, nominally composing the contact alloy. To improve the technology of relay contacts several phases of technological process were examined. Some models of explaining the behaviour of contaminating elements under various experimental conditions such as temperature, sputter-etching process etc are given.

Analiza kontaktnih površin miniaturnih relejev z Augerjevo elektronsko spektroskopijo

Ključne besede: kontakti električni, releji miniaturni, kakovost kontaktov, čiščenje površin kontaktov, jedkanje ionsko, procesi naprsevalno-jedkalni, AES analize, AES Auger spektroskopija elektronska, sestava površin kontaktov, zlitine kontaktne, nečistoče zlitin, detekcija nečistoč

Povzetek: S spektroskopijo Augerjevih elektronov smo studirali strukturo površine kontaktov miniaturnih električnih relejev. Poleg zlata, _eleza, niklja in kobalta, ki sestavljajo kontaktno zlitino, smo detektirali presenetljivo velike količine nečistoč: ogljika, _vepla, kisika in kalcija. Z namenom, da bi izboljšali tehnologijo relejskih kontaktov, smo raziskovali različne faze tehnološkega postopka. Podajamo nekaj modelov, s katerimi razlagamo obnašanje elementov nečistoč pod različnimi eksperimentalnimi pogoji, kot so temperatura, proces ionskega jedkanja itd.

I. INTRODUCTION

Few data have appeared in the literature on the composition of the first few layers of any contact material. Therefore in our research in development of contacts we are interested in finding out the composition of these layers because they dictate the behaviour of contacts.

The Auger electron spectroscopy was chosen to establish the surface composition of contacts since it provides qualitative and semiquantitative information about elements in the upper three to five atomic layers. Only hydrogen and helium can not be detected /1-6/. The Auger peak to peak height, i.e. the distance between the positive and negative extreme of an Auger line in the dN/dE plot versus energy is in first approximation proportional to the element concentration /7/, though the sensitivity is not the same for all elements.

The contacting alloy was composed of gold, iron, nickel and cobalt, and of gold, iron and nickel either. Surprisingly large amounts of contaminants such as carbon, sulphur, oxygen, calcium, silicon and chlorine were detected. To find out the source of these contaminants the relay contacts in various phases in technological process were examined. The results helped us to improve the technology.

II. EXPERIMENTAL

Analyses were performed on the Auger system /2,5,6/ manufactured by Physical Electronics Industries, using a cylindrical mirror analyser with a coaxial electron gun. The diameter of the electron beam on the target was 0,3 mm. Both surface analysis (AES and sputter-etching) could be performed without moving the specimen.

All relay contacts were analysed after one million of operations at the contact current of 0,1 mA D.C. and at the contact voltage of 6V D.C.. First the relay contact surface was analysed. Then the upper layers were removed by bombardment with argon ions (sputter-etching) at the ionic current of 0,5 μ A per 3,6 mm² area, and fresh surfaces were reanalysed. This procedure was repeated until almost all impurities disappeared from the surface.

III. RESULTS AND DISCUSSION

Figure 1 shows Auger electrons spectrum of the surface from a contact whose initial contact resistance was smaller than 100 mohms, but after one million of operations it was increased to more than 100 mohms. Such contacts are not usable and therefore declared as "bad".

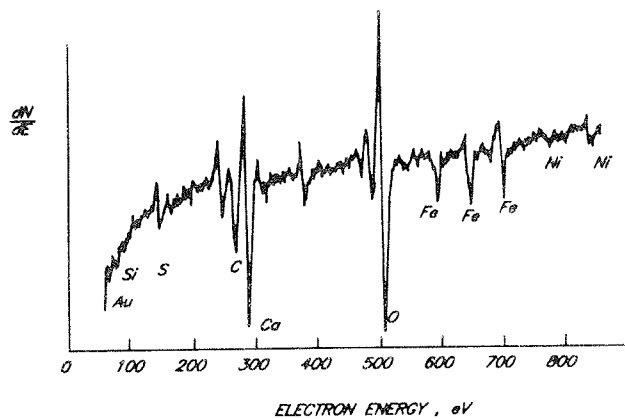


Fig. 1: Auger electron spectrum of the contact surface having contact resistance of 100 mohm.

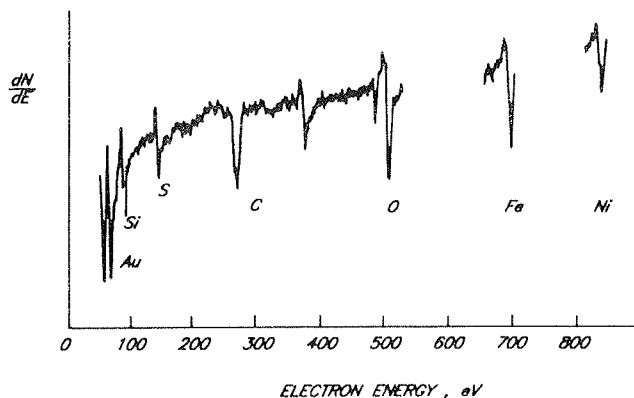


Fig. 2: Auger electron spectrum of the contact surface having contact resistance of 90 mohms.

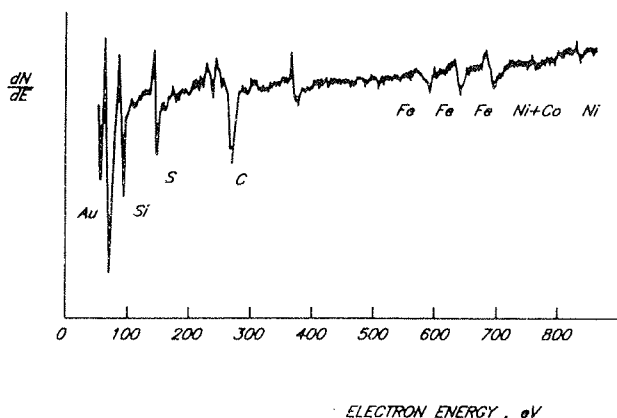


Fig. 3: Auger electron spectrum of the contact surface having contact resistance of 90 mohms.

Gold, the main element of the contact alloy with its characteristic peak at 69 eV is almost unnoticed. Iron at 703 eV and nickel at 848 eV are not observed well, either. However, large amounts of oxygen (at 510 eV), carbon (at 272 eV), sulphur (at 152 eV), and calcium (at

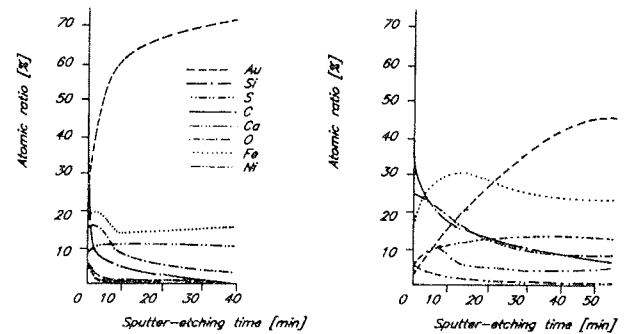


Fig. 4: Composition profile of contact layers with the contact resistance of 90 mohms (1) and 100 mohms (2).

290 eV) are observed, which certainly do not act favourably to the contact properties.

Figure 2 shows the spectrum of surface of a layer contact with the 90 mohm contact resistance after one million of operations, where carbon, sulphur and oxygen appear in relatively small quantities, while calcium does not appear at all. The same is valid also for Figure 3, which shows that there is practically no oxygen at all, while the gold peak is very strong.

The observed trends are even more pronounced when we compare the composition profile of contact layers of two relay contacts after one million operations (Fig.4).

The layer thickness is represented as sputter-etching time. The etching current was 0,5 μ A per 3,6 mm². Concentration of elements was calculated according to:

$$C_x = \frac{I_x \cdot K_x}{I_x^H} \left(\sum_i \frac{I_i \cdot K_i}{I_i^H} \right)^{-1} \cdot 100 \quad (\text{at } \%)$$

where I_x is Auger peak to peak height of the measured element x.

I_x and K_x (scale factor) are obtained from the literature [5].

I_i is the Apph. of the i-th element.

The formula was derived from the following two formulas:

$$C_x = \frac{I_x}{S_{x,Ag}} \left(\sum_i \frac{I_i}{S_{i,Ag}} \right)^{-1} \quad S_{x,Ag} = \frac{I_x^H}{K_x \cdot I_{Ag}^H}$$

Calculating the concentration of sulphur it was taken into account that the gold peak at 150 eV was superimposed on sulphur peak at 152 eV. From the observed peak height the 1/34 of the 69 eV gold peak height was subtracted. We did this since in our experiment the ratio between the peak to peak height in the case of uncon-

taminated gold layers is 1:34 (at 150 eV and 69 eV). Comparing with the literature all the peak to peak heights of gold are approx in the same ratio to 69 eV peak height the one at 150 eV which is 1:17 /5/. We believe that the reason for this is that in the latter case there was some sulphur present as contaminant.

As it is evident from Fig.4, gold is more abundant both on the surface as well as in the internal atomic layers of a contact layer with "gold" contact properties. Carbon and oxygen are also found in smaller quantities. The amount of nickel is approximately equal in all studied samples, but the amount of iron varies to some extent. There is more iron on "bad" contacts. Calcium was found only on "bad" contacts. Small quantities of chlorine and silicon probably do not affect the contact quality.

Many factors which are out of our control influence the height of the signals of Auger electrons of individual elements. Therefore, it is possible that the absolute values of concentrations were somewhat faulty. The exact determination of concentration was not the aim of this work since we were mostly interested in the change of concentration of an element in question in different layers. About 50 contacts were analysed for the composition of contact layers. Even though the composition profiles were not always as pronounced as in the example just given, we found no "good" contact with greater amounts of oxygen, sulphur and calcium on its surface. It is similar for carbon, even it is permissible in greater concentrations. Furthermore it is not definitely established that the surface composition is the only parameter influencing the quality of contacts. Small dust particles and the geometry could also contribute to the enhancement of contact resistance even in the case of good contact composition (no impurities).

Thus, the alloyed golden layer is to some extent covered with impurities. This is unavoidable when working in the atmosphere. We were mainly interested in which technological phase greater amounts of impurities appear on the contact relays, so we might learn which of them must be changed or controlled with greater care.

The contact alloy was made by electroplating of gold on the iron, nickel, cobalt or iron and nickel base, followed by thermal treatment to achieve the diffusion process.

The possible source of calcium atoms is the running water which we use in the technological process.

Sulphur is, opposite to calcium, incorporated in the gold layers. Similar phenomenon was observed in the case when the carbon atoms were incorporated into gold layers /8/.

The composition profile of contact alloy according to Fig.4, shows the decrease of the sulphur concentration in the deeper layers. But after heating by electron bombardment (at $T = 800^{\circ}\text{C}$, few seconds) the presence of sulphur at the surface increased drastically. This is in the agreement with the results presented by the other authors /9/. Regarding the changes noticed in the pre-

vious experiments, the amount of sulphur varied insignificantly by heating unplated contact relays.

The interpretation of this results is rather simple. At the beginning there was some concentration of sulphur present as contaminant bath, from the air pollution /10/ and from the gold plating bath. During the combined sputter-etching and AES analysis the present sulphur atoms were eliminated to the greater extent. After electron bombardment some sulphur atoms from the deeper layers migrated to the surface. As is mentioned above the presence of greater quantities of carbon atoms were also established. We believe that the main source of the carbon atoms is not the gold plating process as we use unbrightened acid cyanide bath. Carbon inclusions in similar electrolytes are known /8,11/, when iron, nickel, cobalt or indium are used as brighteners and are codeposited in the plated layers. In our case atmosphere is also source of carbon atoms /10/.

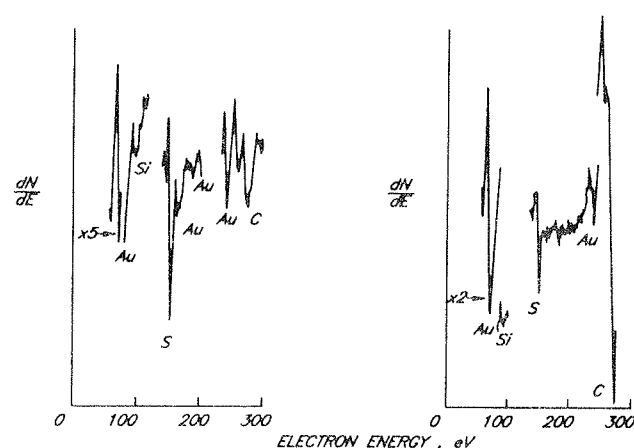


Fig. 5: Auger electron spectra of the surface of the contact relay before (1) and after (2) cleaning with Freon TF.

A noticeable increase of the concentration of carbon (Fig. 5) after cleaning the surface with Freon TF ($\text{CCl}_2\text{F}-\text{CClF}_2$) led us to consider similar method of cleaning with different organic solvents during the technological process is unsuitable. This is in accordance with the data referred in the earlier works /10/.

IV. CONCLUSION

- The analysis of contact surfaces of relay contacts indicated the appearance and the amount of unwanted elements.
- Comparing "bad" and "good" contacts the "good" ones showed greater concentration of gold on the surface as well as in deeper layers. The quality of the contacts depends on the concentration of contaminants such as carbon, sulphur, oxygen, and calcium. The higher the concentration the worse are the properties of the contacts.

- We were interested to find out the sources of the particular contaminants during the technological process. For sulphur it is the gold plating process. The sulphur atoms can not be removed from the surface since in our opinion they are incorporated in the contact alloy.
- Calcium atoms as contaminants originate from running water used in technological process for rinsing after electroplating.
- The sources for contamination of the surface with carbon atoms are the cleaning process with Freon TF, and probably also the relay capsule atmosphere. Unlike sulphur, carbon atoms are not incorporated in the contact layer and can be removed by heating to temperatures higher than 800° C.
- Cleaning with different organic solvents during the technological process is under question for same reason as mentioned above.
- The information like composition and concentration of particular elements at the surface and in the bulk of contacts are necessary for further development in the research and production of contacts. Auger electron spectroscopy is obviously an appropriate method for such investigations. Even more information about contacts could be obtained by using the Scanning Auger Microprobe, which makes possible the analysis of the contact spot with the diameter in the range 30-100 µm.

V. REFERENCES

- /1/ P.W. Palmberg, J. Vacuum Sci. Technol., **9** (1981) 160.
- /2/ C. Chang, Surface Sci., **25** (1981) 53.
- /3/ T. Gallon, Rev. Phys. Technol., **3** (1982) 31.
- /4/ Haas, J. Appl. Phys., **43** (1982) 1853.
- /5/ P.W. Palmberg, G.E. Riach, in Handbook of AES, Physical Electronics Industries, Inc., Edina Minn. (1982).
- /6/ P. Braun, Microchimica Acta, **5** (1984) 365.
- /7/ S. Hoffmann, L.J. Gauckler, Powdering Metallurgy International, **6** (1984) 2.
- /8/ L. Holt, R.J. Ellis, Plating, **60** (1983) 910.
- /9/ R. Kunimori et al., Surface Sci., **46** (1984) 567.
- /10/ M. Antler, Proc. of the 19-th Ann. Seminar on Electronic Contact Phenomena, Chicago, Illinois Institute of Technology, (1983) 20.
- /11/ T.A. Davies, P. Watson, Plating, **60** (1983) 1138.

*L. Koller, dipl.ing., B. Praček, dipl.ing.,
S. Vrhovec, dipl.ing., D. Raišč, dipl.ing.,
Institut za elektroniko in vakuumsko tehniko,
Teslova 30
61000 Ljubljana, Slovenija
tel. +386 61 1231 341
fax + 386 61 263 098*

Prispelo (Arrived): 30.01.95

Sprejeto (Accepted): 24.02.95