UDK621.3:(53+54+621+66) ISSN0352-9045

CLEANING OF THIN PASSIVATION LAYERS ON THE Ag CONTACT MATERIAL WITH VACUUM OUTGASSING

L. Koller[1], M. Bizjak[2], B. Praček[3]
[1]Institute for Electronics and Vacuum Techniques, Ljubljana, Slovenia
[2]Iskra - Stikala, Kranj, Slovenia
[3]ITPO, Ljubljana, Slovenia

Keywords: electrical contacts, material for electrical contacts, surface treating, surface protection, passivation thin films, vacuum outgassing

Abstract: Metallic silver is relatively soft material and a good electric conductor. Therefore it is very suitable material for electric contacts. However, because silver is not resistant to the atmosphere containing H_2S, SO_2 and Cl_2, the surface of the silver contact material must be protected. Well known surface protection with the thin gold layer is too expensive to be economical. In our study we considered some cheaper passivation thin layers which could prevent the corrosive effects of the environment and at the same time assure good electric contact. We chose three different types of passivation thin layers. The first one was deposited by waxing in the Silverbrite solution, for the second layer chromizing was used while the titanium nitride layer was deposited by sputtering. The contact material used was AgNi0,15. Beside electrical properties of the material its clean surface is very important to achieve good electric contact and low level of contact resistance. In the high vacuum outgassing equipment designed and developed in our laboratory samples of silver contact material were outgassed for 48 hours in high vacuum ($1x10^{-7}$ mbar) at 200°C. Analysis of the outgassed substances with the quadrupole mass spectrometer showed that the outgassing rates of all the three passivation layers were low while the composition depended on the type of the layer. Then the thin layers were analyzed with the Auger electron spectroscopy.

Čiščenje tankih pasivacijskih prevlek na Ag kontaktnem materialu z vakuumskim razplinjevanjem

Ključne besede: kontakti električni, materiali kontaktov električnih, obdelava površinska, zaščita površin, plasti tanke pasivacijske, razplinjevanje vakuumsko

Izvleček: Srebro je dobra električno prevodna in sorazmerno mehka kovina. Zaradi tega je po elektromehanskih lastnostih primerna za električne kontakte. Ker pa je neobstojno v atmosferi s primesmi H_2S, SO_2 in Cl_2, je treba kontaktni material površinsko zaščititi. Izbrali smo tri pasivacijske zaščitne prevleke (prva je bila nanesena z voskanjem v raztopini SILVERBRITE, druga s kromatiranjem, tretja, titannitridna, pa je bila napršena) in jih nanesli na kontaktni material AgNi0,15. Za dober električni kontakt in nizko kontaktno upornost je poleg električnih lastnosti zelo pomembna tudi čista površina kontaktnega materiala. V laboratorijski razplinjevalni napravi, razviti doma, smo vzorce pasiviranega srebrnega kontaktnega materiala razplinjevali v visokem vakuumu $1x10^{-7}$mbar pri temperaturi 200°C. Analiza razplinjenih substanc je pokazala, da je velikost razplinjevanja vseh treh zaščitnih prevlek majhna, koncentracija plinskih nečistoč pa je odvisna od zaščitne plasti same. Nanose tankih zaščitnih prevlek po visokovakuumskem razplinjevanju smo analizirali še s spektrometrom Augerjevih elektronov.

1 Introduction

Recently the properties of the outgassed materials /1-3/ hermetically encapsulated into the electronic components attracted considerable attention. One of the main reasons for the failures of the electronic components is the surface contamination /4-7/ of the electric contacts. Contamination film increases the contact resistance and deteriorates the reliability of an electronic component. The most common contamination films are the oxides formed during the termal diffusion and outgassing processes. Besides oxide films the corrosion products and particles resulting from wearing are the main sources of contamination. The growth of industrialization together with the air pollution encounter the problem of the contact sulfating. The specific resistance of Ag_2S ranges from 10^3 Ωcm to 10^8 Ωcm at the room temperature (silver sulfide decomposes at about 300°C) so the sulfating of contacts increases the contact resistance. Contacts may be protected by thin gold plating but there are cheaper passivation coatings, too. We studied the outgassing properties of three possible useful protective thin layers on the contact surface of silver (AgNi0.15) contact material in order to decrease the influence of the surrounding atmosphere. All three layers were outgassed in high vacuum at the increased temperature. The mass spectrometer was used to determine the composition of the outgassed products. Purity and the composition of the protective layers were determined by the Auger spectroscopy.

2 Experimental

To protect the silver based contact material AgNi0.15 three different types of thin layers were used:

- Passivation by waxing. Test samples were treated in the water solution named Silverbrite /8/.
- Passivation by chromizing. Layers were made by anode oxidation according to the receipt /9/.
- Passivation by solid layer. Solid layer Ti/TiN was formed by sputtering /10/.

All the passivation thin layers were outgassed in high vacuum $1x10^{-7}$ mbar at the temperature 200°C 48 hours in the vacuum outgassing comora /11/. Products of the outgassing procedure were analysed with the quadrupole mass spectrometer (masses from 1 to 100) TRANSPECTOR GAS ANALYSIS SYSTEM - MODEL C100, F LEYBOLD Inficon Inc. Mass spectra were taken twice: after half an hour and after 48 hours of outgassing. Purity and composition of three surface layers after the outgassing were determined by the Auger spectroscopy (AES). AES spectrometer /12/ (PEI, SAM, Model 545A) with the static primary electron beam with the energy of 3 keV, the beam current of 0.5 μA, and the beam diameter of about 40 μm was used for the analysis. Etching was performed on the surface area of 10 mm x 10 mm with the two Ar^+ ion beams with the energy of 1 keV. The incidence angle of the ion beam was 47°. The etching velocity was about 1.7 nm/min and was calibrated with the standard Ni/Cr sample. For determining the element concentration (except for the nitrogen concentration where the factor was calculated from the standard sample of stehiometric TiN) the sensitivity factors were taken from the spectroscope manufacturer (PEI) manual.

3 Results and discussion

The composition of gasses evaporated out of the heated surface of samples made of the passivated contact material AgNi0.15 is presented in mass spectra in Figures 1 to 6. Mass spectra of the outgassed products from the silver contact material AgNi0.15 coated with the thin passivation layer in the Silverbrite solution are presented in Fig.1 after 30 minutes and in Fig. 2 after 48 hours of outgassing, respectively. Spectrum in Fig. 2 shows that after 48 hours of outgassing at 200°C and at the total pressure $2x10^{-7}$ mbar nearly all the evaporable contaminants and hydrogen H_2 are removed. The same conclusion can be drawn for the outgassing of cromated contact material (Figures 3 and 4). When the contact material AgNi0.15 was passivated by the solid layer Ti/TiN (mass spectra in Figures 5 and 6) greater amount of contaminants than in the first two cases is noticed on the surface before the beginning of the outgassing. After the 48 hours of outgassing at 200°C the contaminants are not removed completely. At the same time the strong hydrogen peak is observed. During the procedure of sputtering considerable amount of molecules are built in the protective layer. Also, when the procedure of sputtering is finished the

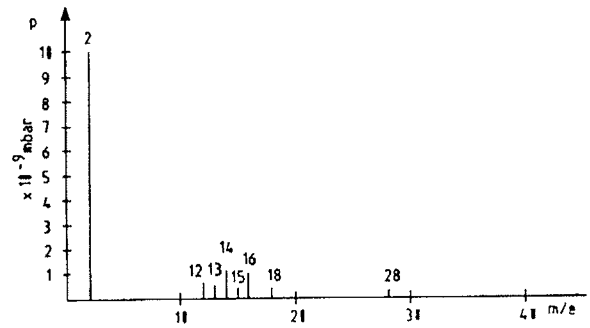

Figure 3. Mass spectrum of the outgassed products from the cromated silver contact material AgNi0.15 after 30 minutes of ougassing ($4x10^{-7}$ mbar, 25°C).

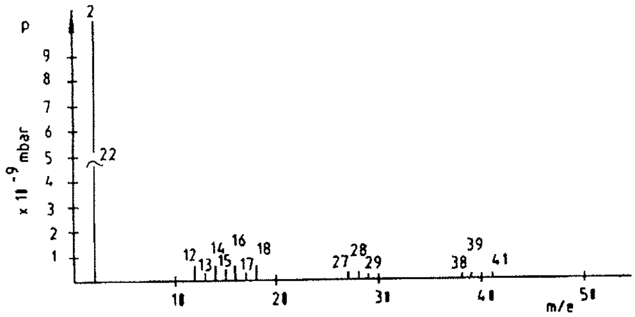

Figure 1. Mass spectrum of the outgassed products from the silver contact material AgNi0.15 waxed in the Silverbrite solution after 30 minutes of ougassing ($2x10^{-7}$ mbar, 25°C).

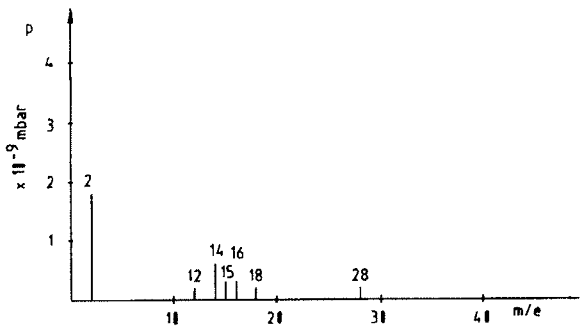

Figure 4. Mass spectrum of the outgassed products from the cromated silver contact material AgNi0.15 after 48 hours of ougassing ($1.8x10^{-7}$ mbar, 200°C).

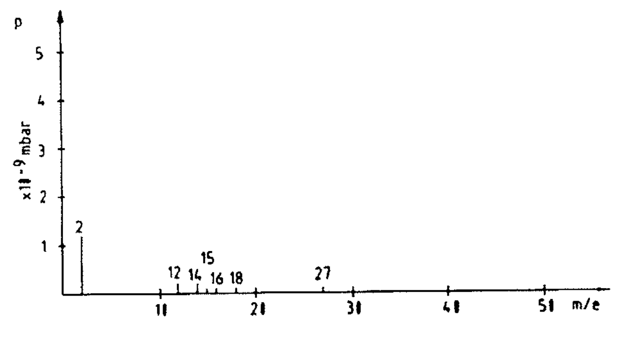

Figure 2. Mass spectrum of the outgassed products from the silver contact material AgNi0.15 waxed in the Silverbrite solution after 48 hours of ougassing ($2x10^{-7}$ mbar, 200°C).

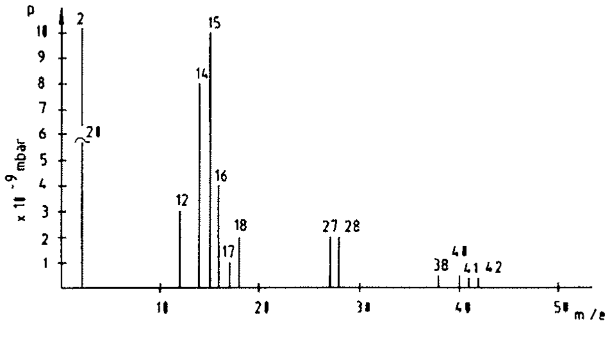

Figure 5. Mass spectrum of the outgassed products from the sputtered silver contact material AgNi0.15 with the titanium nitride Ti/TiN after 30 minutes of ougassing ($8x10^{-7}$ mbar, 25°C).

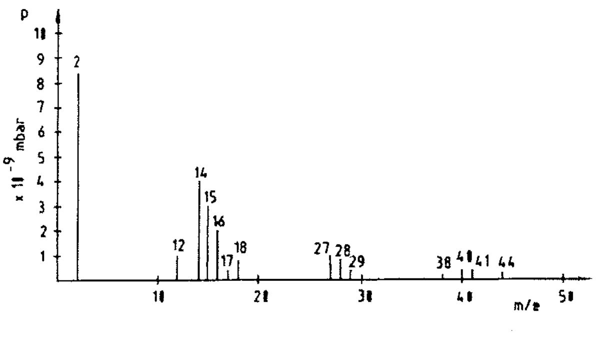

Figure 6. Mass spectrum of the outgassed products from the sputtered silver contact material AgNi0.15 with the titanium nitride Ti/TiN after 48 hours of ougassing ($4x10^{-7}$ mbar, 200°C).

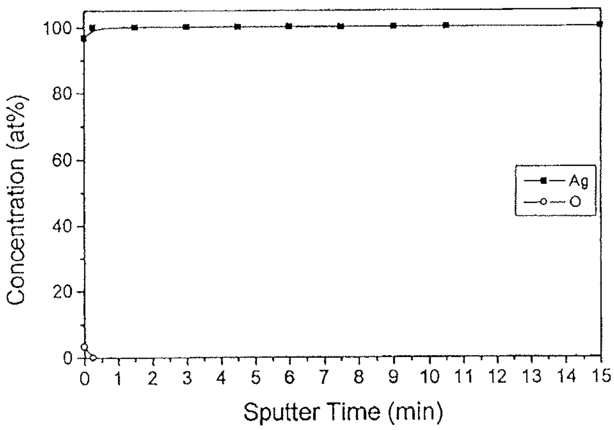

Figure 7. Profile diagram of the silver contact material AgNi0.15 waxed in the Silverbrite solution after the outgassing.

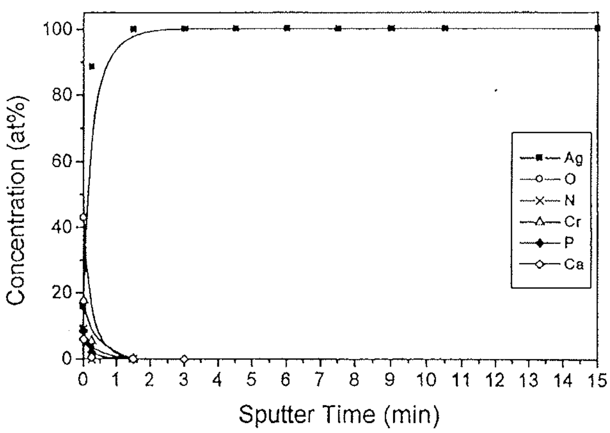

Figure 8. Profile diagram of the cromated silver contact material AgNi0.15 after the outgassing.

protective layer is rather active so that larger amount of gas can be absorbed. Contamination of the layer depends very much on the technology of the procedure. Results of the AES analysis as three profile diagrams are presented in Figures 7, 8 and 9. Profile diagrams of

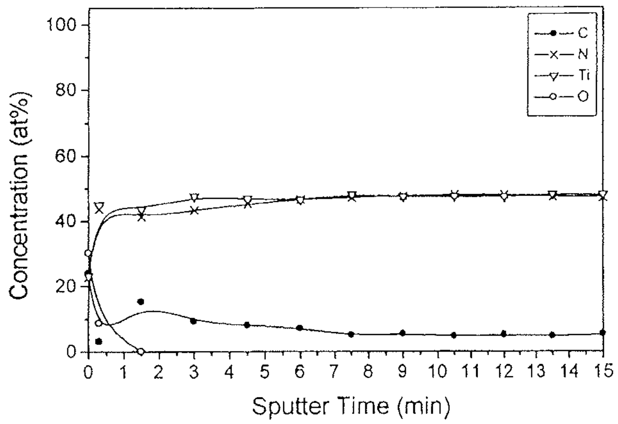

Figure 9. Profile diagram of the sputtered silver contact material AgNi0.15 with the titanium nitride Ti/TiN after the outgassing.

the waxed silver contact material AgNi0.15 (Fig. 7) after the outgassing shows the extremely clean surface with just the traces of oxygen. Profile diagram of the cromated silver contact material AgNi0.15 (Fig. 8) after the outgassing shows the passivation layer which is less than 1 nm thick and consists mainly of chromium with small concentrations of nitrogen, phosphorus and calcium on the surface. The surface is oxidized to a great deal while there is no oxygen inside the layer. Profile diagram of the silver contact material AgNi0.15 passivated by the Ti/TiN solid layer (Fig. 9) after the outgassing shows that titan nitride layer is slightly oxidized only at the surface. Inside the layer the carbon incorporated during the formation of the layer is detected.

4 Conclusions

Outgassing properties of three conducting passivation thin layers on the silver contact material AgNi0.15 are studied. First passivation layer was deposited by waxing in the Silverbrite solution, the next one by chromizing using the electrochemical procedure, while the third one (Ti/TiN) was deposited by sputtering.

Outgassing was performed in high vacuum ($1x10^{-7}$ mbar, 200°C, 48 hours), the mass spectrometer was used to determine the composition of the outgassed products. Thin passivated protective layers after the outgassing was studied with the use of the Auger spectroscopy.

Our studies show that all the three passivation thin layers considered are suitable for protection of silver contact material. The layers produced are very clean with low outgassing rate and are not expensive.

5 References

/1/ M Wutz, H Adam, W Walcher, in Theory and Practice of Vacuum Technology, Friedr. Vieweg & Sohn, Braunschweig/Wiesbaden, 1989.

/2/ L Koller, M Jenko, S Spruk, B Praček, S Vrhovec, Vacuum, 1995, 46, 827.

/3/ L Koller, S Vrhovec, M Jenko, Kovine, zlitine, tehnologije, 1995, 29, 515.

/4/ R Holm, in Electric Contacts Handbook, Springer, New York, 1967.

/5/ M Bizjak, L Koller, K Požun, J Leskovšek, ICEC'98 Offenbach, VDE-Verlag 1998, 47.

/6/ SK Chawla, JK Payer, J. Electrochem. Soc., 1990, 137.

/7/ J Schirnikat, H-J Gewatter, L Kiesewetter, F & M 1996, 104, 515.

/8/ Doduco Datenbuch, 2. Aufl. Pforzheim, 7, 1997.

/9/ Navodilo za uporabo "Cromating AG-797100", Kemična tovarna Podnart.

/10/ B Navinšek, P Panjan, J Krušič, Service and Coating Technology, 1998, 98, 809.

/11/ L Koller, M Bizjak, K Požun, Kovine, zlitine, tehnologije, 1999, 32, 155.

/12/ B Praček, Kovine, zlitine, tehnologije, 1996, 30, 53.

Lidija Koller, univ. dipl. inž. kemije
Inštitut za elektroniko in vakuumsko tehniko
Teslova 30
1000 Ljubljana
številka raziskovalca:1703
tel. 061/177-66-58
faks 061/126-45-78
E-pošta: joze.koller@uni-lj.si

domači naslov:
Cesta na Laze 15
1000 Ljubljana
tel. 061 / 159-7661

Dr. Martin Bizjak, univ. dipl. inž. fizike
Iskra - Stikala,
4000 Kranj
številka raziskovalca: 3930
tel. 064/37-22-26
faks 064/37-22-59
E-pošta: iskra.stikala-rd@siol.net

domači naslov:
Sveti Duh 275,
Škofja Loka
tel. 061/159-7661

B. Praček, univ. dipl. inž. metalurgije
Inštitut za tehnologijo površin in optoelektroniko,
Teslova 30,
1000 Ljubljana
številka raziskovalca: 9105
tel. 061/126-45-92
faks 061/126-45-93

Prispelo (Arrived): 01.02.00 *Sprejeto (Accepted): 27.03.00*