ELECTROCHEMICAL DEPOSITS OF GOLD IN TRANSISTOR ASSEMBLING PROCESS

M. Gojo
Faculty of Graphic Arts, Zagreb, Croatia
N. Cikovic
Faculty of Food technology & Biotechnology, Zagreb, Croatia

Key words: transistor assembling, electrochemical deposits, gold deposition, gold coating, AES analysis, SEM, scanning electron microscope, SEM analysis, Au-Si eutectic alloy

Abstract: A montage of semiconductive components on metal basements in the electronic industry is of the great practical importance. For this purpose the process of electrochemical deposition of gold on the backside of silicium wafer consisting of Au-Si eutectic alloy has been developed.
The process of electrochemical deposition of gold from citrate solutions containing thalium ions is studied on rotating disc electrode using cyclic voltametry the method polarization.
Structure and morphology of gold coatings are determined by AES and SEM methods of analysis.
Gold deposits were observed to be of bright yellow-gold colour and of small-size grain. In the presence of Tl^+ ion was possible to achieve higher current density of gold deposition, but the current rise had no consequences on the grain size.
The chemical composition of Au-Si eutectic alloy had no greater influence on the electrochemical process thus the electrochemical deposition of gold was equal to that one on the pure gold background.

Elektrokemijske prevlake zlata u procesu montaže tranzistora

Ključne riječi: montaža transistorjev, nanosi elektrokemični, nanašanje zlata, prevleke zlate, AES analize, SEM mikroskopi elektronski skanirni, SEM analize, Au-Si zlitina eutektična

Sažetak: Za potrebe montaže poluvodičkih komponenti na metalna podnožja u elektroničkoj industriji razvijen je proces elektrokemijskog taloženja zlata na stražnju stranu silicijeve pločice koja se sastoji od eutektika zlato-silicij.
Metodom cikličke voltametrije, na rotirajućoj disk elektrodi, ispitivali su se elektrokemijski procesi taloženja zlata iz citratnog elektrolita bez i s dodatakom talij (I) nitrata različitih koncentracija.
Struktura i morfologija dobivenih prevlaka zlata određena je AES i SEM analizom.
Dobivene prevlake zlata su plošno centrirane sitnozrnate strukture sjajne zlatno-žute boje. Dodatak talija omogućuje povećanje gustoće struje, no to povećanje ne uzrokuje promjenu strukture taloga.
Kemijski sastav eutektika zlato-silicij nema značajnijeg utjecaja na elektrokemijski proces, odnosno elektrokemijsko taloženje odvija se kao taloženje zlata na zlatu.
Montirani uzorci pokazuju visoki postotak zalegiranosti bez obzira na kemijski sastav i strukturu eutektika zlato-silicij.

1. INTRODUCTION

20 μm gold preform (a thin band of gold with a 0.5 wt% silicon) is used in semiconductor industy for the purpose of assembling semiconductive components

In the process of assembling, the preform is cut into small wafers that are put between the heated basement and a semiconductive element. An electrochemical deposition of pure gold whose properties and thickness allow good assembling was performed on the back-side of a monocrystal wafer containing a layer of vacuum vapoured and alloyed gold; the aim was to reduce the waste as well as to increase productivity and save the precious material.

In order to be applied in semiconductive technology, a gold deposit, apart from the process of gold deposition itself, must fulfil some specific technological requirements such as mechanical properties, eutectic bonding and the purity of gold deposits.

2. EXPERIMENTAL

Samples used in the experiments of cyclic voltametry, AES and SEM analysis as well as in examining the quality of eutectic bonding were prepared from monocrystal silicon wafers of crystalographic orientation (111) and (100). On the frontside of silicon wafer there were active semiconductive components, while on the backside there was a thin layer of gold which has been previously deposited using vacuum vaporization method and then alloyed at 703 K. In all the experiments of cyclic voltametry and elecrochemical deposition of gold, the electrolyte used was a citrate solution containing:

di-basic amonium citrate: $C_6H_{14}N_2O_7$, 50 gdm^{-3} (0.22 $moldm^{-3}$)

potassium gold(I) cianide, $KAu(CN)_2$, 20 gdm^{-3} ($6.94x10^{-2}$ $moldm^{-3}$)

talium(I) nitrate, $TlNO_3$, $3.75x10^{-4}$ $moldm^{-3}$

pH of the elektrolyte was from 5.8 to 6.2.

All the chemicals used were of p.a. purity /1/.

In order to protect the prepared semiconductive components and aluminium contact from the influence of the electolyte, the frontside of the silicon wafer was protected. Satisfactory results of protection were obtained by SHIPLY's pozitive photoresist AZ 1350 J which was applied on the wafer /2/.

Experiments were done in the presence of nitrogen at 343 K. The polarization rate was 20 mVs^{-1} and the potential values were changed from the steady state potential value of +95 mV to -1000 mV. The electrode rotation speed was 500, 750, 1000, 1250, 1500, 1750 and 2000 min^{-1}. The purity of the gold deposits was determinated by AES analysis.

The deposit was etched by argon ions (Ar^+) until the Au-Si interface was reached. In profile analysis, the following parameters were used:

energy of the primary electrone beam 3 keV, electron current 0.5 μA, and the diameter of the electrone beam 40 μm. The ionic etching of the sample was performed by use of the argon ions stream. The applied energy was 1 keV, the ion current intensity 6.8 nA, the angle of incidence 47°. The surface area of the sample was 5 x 5 mm.

Chips with the electrochemically deposited gold were installed on the nickel- plated basements of the type TO 18 and TO 39. The assemling was performed on a semi-automatic machine under following working conditions:

- the temperature in the tunnel: zone A 793 K; zone B 793 K
- the gas flow N_2: zone A 2.5 dm^3min^{-1}; zone B 1.5 dm^3min^{-1}
- H_2: 0.70 bars
- forming: zone A 20 % H_2; zone B 15 % H_2
- the passage rate through the tunel: 2 basements per minute

The research of eutectic bonding was done by a destructive test of plucking the chips from the basement and the criterion of a good eutectic bonding was that minimum 75 % of silicon surface of the chip must remain on the basement.

3. RESULTS AND DISCUSSION

3.1.Polarization Measurements

The elecrochemical deposition of gold on a gold - silicon surface was studied using the cyclic voltametry polarization method.

Figure 1. shows the voltamograms of electrode polarization in citrate solution free from thalium. Starting from the steadystate up to the potential of -700 mV, a small increase of current density was observed while a dependence on the electrode rotation speed has not been noticed.

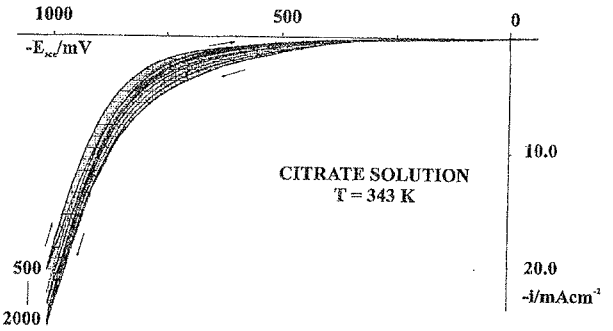

Fig. 1. Voltamograms of chatodic polarization free from thalium

After the potential of -800 mV, the current density was increasing more rapidly and a small dependence on the rotation speed occurs. The reverse branch of the polarization curves follows the starting branch, only the current density is smaller.

The addition of $TlNO_3$ in to the citrate solution considerably changes the electrochemical conditions of gold deposition (fig. 2).

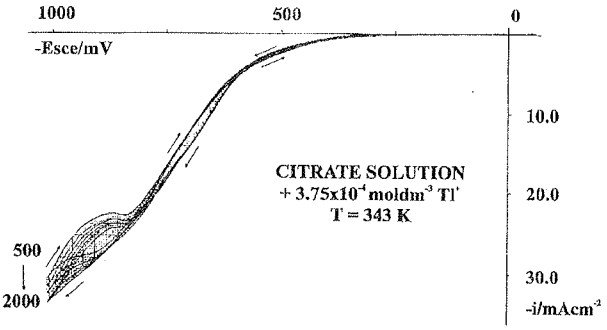

Fig. 2: Voltamograms of chatodic polarization in the presence of thalium

Voltamograms of chatodic polarization of Au-Si eutectic show a slow increase of current density on the starting branch of curves, beginning from the steadystate potential value of +100 mV up to the potential of -300 mV. After this potential, current density begins to increase significantly. At the potential value of -750 mV an inflection occurs after which the increase of current density is not so significant. On the revers branch of polarization curves, the decrease of current density is greater than on the starting branch, in the same area of potential. At -800 mV a stagnation of current density occurs. With the following decrease of the potential, the current density rapidly decreases until -500 mV, then the decrease is somewhat slower until the steadystate potential value is reached.

Voltamograms also show a slight dependence of current density on the electrode rotation speed on both starting and reverse branch of polarization curves as from the potential of -500 mV. The dependence is especially distinct in the area of current stagnation (- 800 mV to -1000 mV), which is due to the change of the reaction mechanism in the presence of thalium.

3.2. AES Analysis of Gold Deposits

By examining electrochemical deposits of gold obtained from citrate electrolyte at 343 K, with applied current density of 1.5 $mAcm^{-2}$, the profile diagram shows that the surface of the deposit consists of about 80 atomic per cent of gold and about 20 atomic per cent of carbon with small treaces of oxygen and nitrogen. The ionic etching removes these impurities and the pure gold remains (fig. 3).

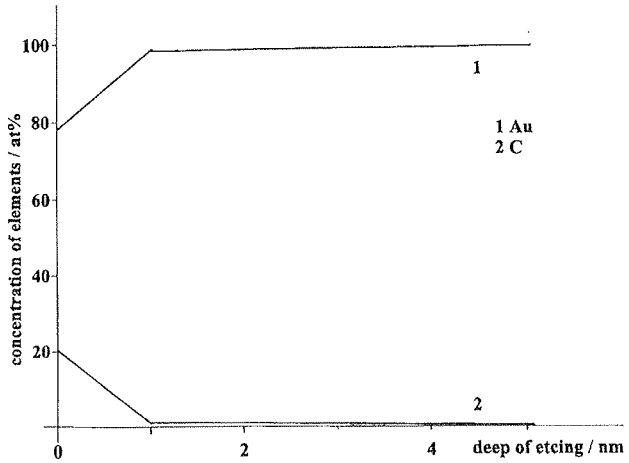

Fig. 3: AES analysis of gold deposit free from thalium

AES Analysis was also preformed on samples obtained from citrate solution containing 3.75 x 10^{-4} $moldm^{-3}$ of thalium, at the temperature of 343 K and the applied current density of 10 $mAcm^{-2}$.

The profile diagram in fig. 4. shows that the surface of the deposit consists of about 80 atomic per cent of gold, 16 atomic per cent of carbon and of impurites in the concentration up to 1 atomic per cent.

By the ionic etching into the inside of the gold deposit up to 1 nm, all the impurities are removed from the surface an the pure gold remains.

The profile diagram (fig. 5) shows clearly that the surface of the sample consists almost of pure gold (99 atomic per cent) and negligible impurities.

By the ionic etching into the inside of sample and through the entire gold deposit, we see that only a pure gold is present in the deposit. When the Au-Si intersurface is reached silicon is registered and its concentration continously increases. Traces of thalium have not been found.

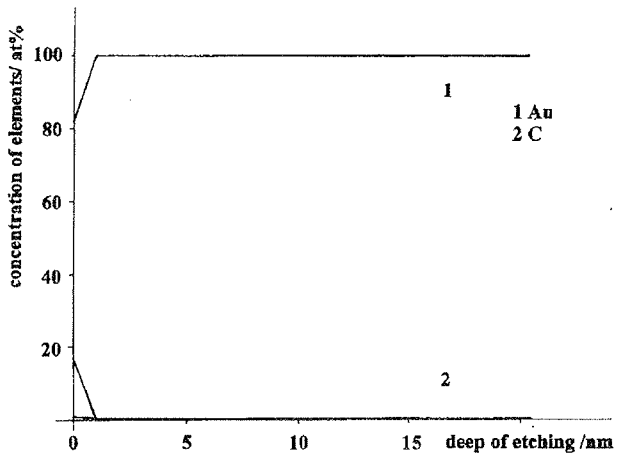

Fig. 4: AES analysis of gold deposit in the presence of thalium

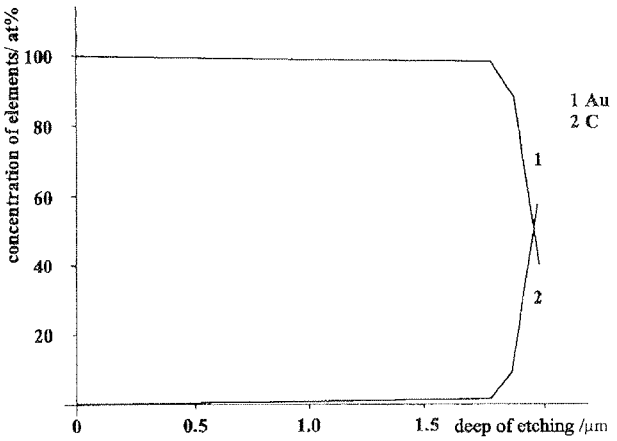

Fig. 5: Profil AES analysis of gold deposit in the presence of thalium

3.3. SEM Analysis of Gold Deposits

Depending on the treatment of the backside of the silicon wafer /3/, the morphology of the gold deposit surface is changed.

The morphology of the surface changes depending on the type of grinding,etching, alloying the vapourized gold and on the electrochemical conditions of the experiment.

After the treatment of the back side of the silicon wafer by etching solution of the composition HF : CH_3COOH : HNO_3 = 1 : 2.5 : 3 and the later vapourizing/alloying of gold a well defined tetrahedronic structure is obtained (Fig. 6).

When an electrochemical deposition of gold is performed on such a surface (experimental conditions: temperature 343 K, current density 1.5 $mAcm^{-2}$, citrate

solution free from thalium) tetrahedrons disappeare and the gold deposit of small size grains is evident (Fig. 7).

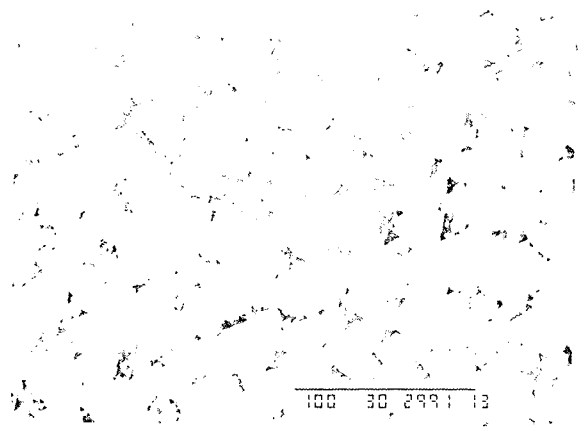

Fig. 6: SEM analysis of the surface silicon wafer with vapourizing and alloying gold deposit

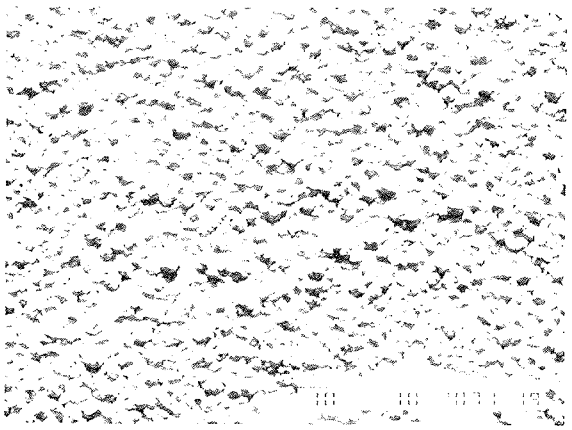

Fig. 7: SEM analysis of gold deposit free from thalium

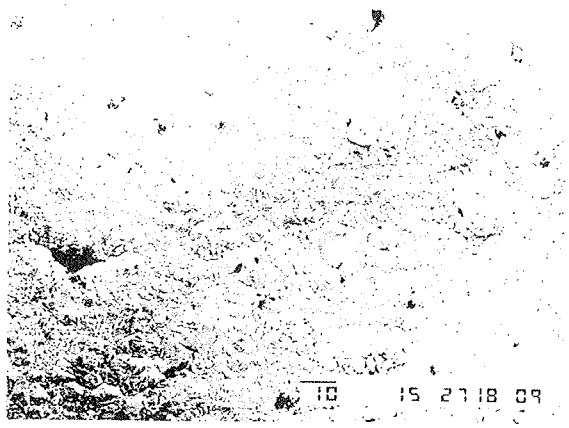

Fig. 8: SEM analysis of gold deposit in the presence of thalium

The addition of 3.75×10^{-4} moldm^{-3} of thaliium into the citrate solution at the same experimental conditions increases to some extend the grain size, but the deposit remains compact and unporous (Fig. 8).

The structure of gold deposit also changes varying the temperature: by the increased temperature the grain size is reduced. The value of the applied current density as well as the concentration of thalium have also a certain effect on the structure of gold deposit. In the presence of thalium and the current density value of 5.0 mAcm^{-2} the gold deposit is still compact and of a fine-grained structure.

Thus depending on the previous treatment of the silicon wafer, the conditions of alloying, the type of the eutectic alloy obtained as well as on the experimental conditions of gold deposition (temperature, current density, stirring) gold deposits of different morphology can be obtained.

3.4. Checking of Eutectic Bonding

A visual analysis of the transistor samples which are assembled on nickel-plated basements of the type TO 18 or TO 39, and which are covered with thin layer of electochemically deposited gold has shown that the eutectic is equally spread all over the surface, it covers well the lateral sides of the chip, the meniscus is of the equal height and it reaches a half of the lateral surface. The chip - basement connection seems to be solid with no indications of bad eutectic bonding, or chip separation from the basement. The eutectic has a regular structure on the chip - basement borderline, and in the part where the eutectic is spread all over the surface of the nickel - plated basement, it looks like fine molten metal. The results of the destructive test of plucking the chip from the basement are shown in table 1:

Table 1: Alloyed of chip without thalium in citrate solution

Sample No:	Eutectic bonding %	Sample No:	Eutectic bonding %
1	100%	14	100%
2	100%	15	100%
3	100%	16	100%
4	100%	17	100%
5	90%	18	100%
6	100%	19	100%
7	100%	20	100%
8	100%	21	100%
9	100%	22	90%
10	100%	23	100%
11	100%	24	100%
12	100%	25	100%
13	100%	26	80%

The addition of thalium into the citrate solution changes the structure of the eutectic, and a visual analysis indicates that it does not cover sufficiently the chip. Such Au-Si chip is an indicator of bad eutectic bonding, but the results show that such an eutectic structure has also high percentage of eutectic bonding (table 2).

Table 2: Alloyed of chip with thalium in citrate solution

Sample No:	Eutectic bonding %	Sample No:	Eutectic bonding %
1	100%	14	100%
2	100%	15	100%
3	100%	16	100%
4	100%	17	100%
5	100%	18	100%
6	100%	19	100%
7	100%	20	100%
8	100%	21	100%
9	100%	22	80%
10	100%	23	100%
11	100%	24	100%
12	100%	25	100%
13	100%	26	100%

4. CONCLUSIONS

References /6/ show that the addition of small amounts of foreign elements into the electrolyte for metal deposition considerably affects the electrochemical process, as well as the structure of the deposits obtained.

The addition of thalium into the citrate solution shifts the potential of the electrochemical deposition of gold towards more positive values, which indicates that a gold deposition is occuring earlier than in the case when thalium is not present in a solution.

At the same time, the addition of thalium makes possible an increasing of the current density, it changes the mechanism of electrochemical deposition of gold due to its catalytic action, it decreases also the activation energy and it has an important influence on electrocrystalization of gold.

The profile AES analysis also indicates the catalytic role of thalium because the presence of thalium is not observed in the gold deposit.

The structure of the deposit also depends on the temperature, current density and the constitution of the electrolyte, which is evident from the morphology of gold deposits.

References /7,8/ prove that different structures of deposits may be obtained from citrate electrolyte, depending on the applied current density and the electrode rotation speed. At smaller values of current density, the gold is configured in face-centered crystal lattice. By increasing current density, the structure of the deposit changes and becomes of the mixed character while at higher values an appearance of peacks is prevailing.

During the electrochemical deposition of gold from citrate solution free from thalium, the maximum current density is about 1.5 $mAcm^{-2}$ at 343 K. The deposit obtained is of small grained face-centered structure, it is of bright yellow colour and fulfil the necessary requirements for semiconductive components.

However, the addition of thalium into citrate electrolyte enables the increase of current density to 5.0 $mAcm^{-2}$ and deposits obtained retain their original colour and structure, and peacks do not appear as it was said in references. The results of eutectic bonding of chips on nickel - plated basements TO 18 and TO 39 indicate that the change in morphology which is caused by the addition of thalium has no effect on the strength of the chip - eutectic - basement link, even the strength is slighly increased. It is obvious that the adsorbtion of thalium on the electrode considerably effects the course of the electrocrystallizaton of gold.

5. REFERENCES:

/1/ M. Gojo, Ph.D. Thesis, University of Ljubljana, Slovenia, (1995).

/2/ M. Gojo, Proc. of Conf. SD '89., Maribor, (1989), 199.

/3/ M. Gojo, M. Petrinec, J. Vuković, M. Turčec, Proc.of Conf. SD '87., Topolšica -Velenje, (1987), 377.

/4/ B. Praček, M. Gojo, Proc. of VI. Yugoslav Vacuum Congress, Gozd Martuljak, (1990), 550.

/5/ M. Gojo, N. Ciković, Proc. of MEET '95, Rijeka, (1995), 2-1.

/6/ J.D.E. McIntyre, W.F. Peck Jr., J. Electrochem. Soc., 123, (1976), 1800.

/7/ H.Y. Cheh, R. Sard, J. Electrochem. Soc., 118, (1971), 1737-1747.

/8/ D.M. MacArthur, J. Electrochemical Soc., 119, (1972), 672.

Dr. Miroslav Gojo, dipl. ing.
Faculty of Graphic Arts,
Univesity of Zagreb
HR 10000 Zagreb, Getaldićeva 2
tel: + 385 1 21 64 44
fax: + 385 1 233 53 97
E-mail: gojo @ magrf.grf.hr.
Prof. dr. Nada Ciković, dipl. ing.
Faculty of Food technology & Biotechnology,
University of Zagreb
HR 10000 Zagreb, Pierottijeva 6
tel. + 385 1 44 00 05, 44 04 22/385
fax: + 385 1 41 82 30
E-mail: ncikov @mapbf.pbfrng.hr

Prispelo (Arrived): 27.5.1996 *Sprejeto (Accepted): 18.6.1996*