IOP Conf. Series: Materials Science and Engineering **229** (2017) 012010 doi:10.1088/1757-899X/229/1/012010

Study on Silver-plated Molybdenum Interconnected Materials for LEO Solar Cell Array

Jia-jun Zhu[1,2,*], Yu-hao Hu[1,2], Meng Xu[1,2], Wu-lin Yang[1,2], Li-cai Fu[1,2], De-yi Li[1,2] and Ling-ping Zhou[1,2]

[1] College of Materials Science and Engineering, Hunan University, Changsha 410082, China

[2] Hunan Province Key Laboratory for Spray Deposition Technology and Application, Hunan University, Changsha 410082, China

*spolestar@163.com

Abstract. Atomic oxygen (AO) is one of the most important environmental factors that affected the performance of low earth orbit spacecraft in orbit. In which, silver was the most common materials as the interconnected materials. However, with the poor AO resistance of silver, the interconnectors could be failure easier , and the lifetime of the spacecraft was also reduced. In this paper, the silver-plated molybdenum interconnected materials made by Ag thin films deposited on the Mo foils by vacuum deposition methods was studied. And the effects of the preparation process on the micro-structure of the Ag thin films, the interfacial adhesive strength and the electrical conductivity of the composites were investigated. It was found that the Ag thin films deposited on the Mo substrates coated the Ag thin films by ion beam assisted deposition(IBAD) methods exhibited a perfectly (200) preferred orientation. The interfacial adhesive strength had been increased to 18.58MPa. And the composites also have excellent electrical performance .

1. Introduction

All spacecraft in low Earth orbit (LEO, defined for altitudes between about 200-1000km), such as space shuttle, International Space Station, reconnaissance satellite, navigation satellite, are affected by different components of the LEO environment. The LEO space is a complex and dynamic environment that was consisted of high vacuum, radiation, temperature extremes, atomic oxygen(AO), charged particles, micrometeoroids, and man-made debris, which may severely affect the lifetime of the spacecraft. Among them, AO is the predominant and the most active component of LEO atmosphere. When the spacecraft is flying in LEO at an orbital velocity of 7.8 $km \cdot s^{-1}$, AO flux has impingement kinetic energy of about 3-5eV. At this energy, AO would initiate some chemical and physical reaction with the surface materials on spacecraft.[1-3].

So that, for LEO applications, the solar cell interconnectors have to sustain extremely high fatigue cycles and be subjected to the AO environment. It is well known that silver was one of the earliest interconnected materials for space solar cell panels. And the thickness of silver foil is approximately 30μm. However, in the case of silver, the AO reaction rate is about $10.5\times10^{-24} cm^3 \cdot atom^{-1}$[4], so a very high fraction of the incident AO reacts with the silver to form silver oxide. As figure 1 shows that the silver interconnectors from Eureca Program, the silver layer oxidized by atomic oxygen was flaked off. Due to the thermal stresses, the oxide layer exposing underlying fresh material, it continuously breaks up. One way to protect the silver of being oxidized by AO is by plating with gold. But as illustrated by figure 2, still a lots of pin-holes under the gold plating were created and silver-oxide was found at the surface[5]. So the average lifetime of the spacecrafts was only about 1-3 years.

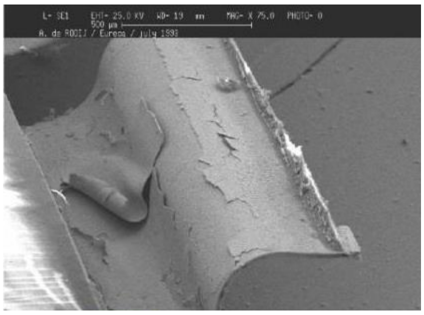

Figure 1. Silver interconnected materials from Eureca.

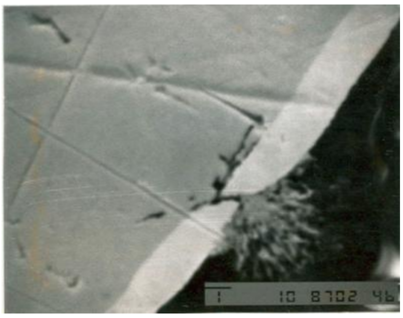

Figure 2. The pin-holes under the gold-plated silver foils.

For such extreme conditions, the interconnectors consist preferably of Kovar/lnvar [6-7]or molybdenum with applied silver coatings to allow welding, because of the good match of coefficients of expansion to silicon and, consequently, the relative lower incidence of cracks in the joints. But Kovar or Invar is ferromagnetic, which could induce some negative effects for space application. In comparison, molybdenum is still AO-resistant for its AO reaction rate about $1.4\times10^{-27}cm^3\cdot atom^{-1}$. The European Space Research Organization had performed resistance welding (parallel-gap) using silver-plated molybdenum(Ag/Mo) interconnectors, and no damage was found in temperature cycling test[8].

However, in the case of binary immiscible Ag-Mo system, which has an extremely large positive ΔHf being +57 kJ/mol. The interfacial adhesive strength between the Ag films and Mo substrate made by electroplating directly was very low. In this case, the metal transition layer was often needed to improve the adhesive strength, hence the process was complicated and the reliability of the materials was not high. Yuan HUANG[9] had researched that Ag/Mo composites was prepared by irradiation damage alloying method on Mo base. And the amorphous alloy layer was formed on the surface of the Mo base. In this paper, the Ag thin films deposited on the Mo substrates coated the Ag thin films by ion beam assisted deposition(IBAD) methods exhibited a perfectly (200) preferred orientation, while enhancing the adhesive strength of Ag/Mo interface greatly.

2. Experimental details

2.1. Deposition conditions

The deposition of Ag films was performed on homemade deposition system. Two Kaufman ion sources were set in the chamber as shown in figure 3(a), one of them called sputtering ion resource was used for sputtering an Ag target (purity >99.99%) with 1200eV Ar^+ ions, the other called assisted ion resource was used for bombarding the growing films with 30keV Ar^+ ions. And the assisted ion beam was incident along normal direction of film surface. The Magnetron sputtering devices were also installed in the same chamber as shown in figure 3(b).

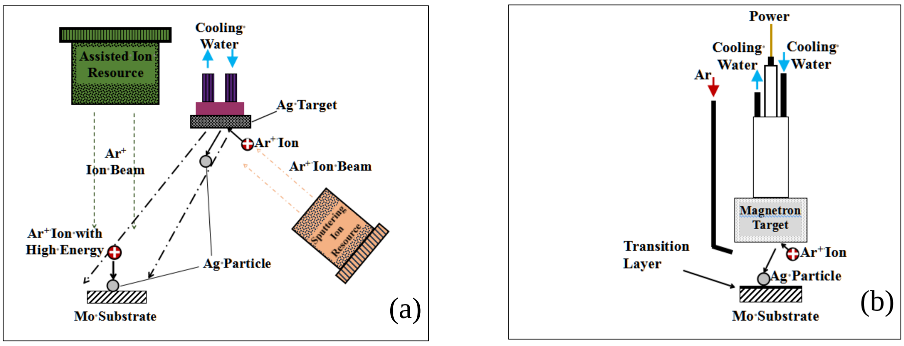

Figure 3. Schematic diagram of the Ag thin films deposited on Mo fiol by（a）ion beam assisted deposition（b）magnetron sputtering deposition

The Ag thin films was deposited on 12μm-thick Mo foil substrates by three sputter methods, which are ion beam sputtering deposition(IBD), ion beam assisted bombardment deposition(IBAD) and magnetron sputtering deposition(MD), respectively. The deposition method of Ag thin films only using sputtering ion resource without assisted ion resource was named IBD. The deposition of Ag thin films using sputtering ion resource, while the growing films were bombarded by assisted ion beam, which was named IBAD. Pure Ag (purity>99.99%) was used as a target materials, and the purity of argon as working gas was about 99.999%. The deposition chamber was evacuated to a background vacuum pressure of less than 5×10^{-4} Pa. The process parameters of deposited Ag thin films are shown in table 1. Before deposition, the surface of Mo foils was cleaned by 0.7keV and 60mA low energy ion beam about 15 minites.

Table 1. The process parameters of deposited Ag thin film

Assisted ion resouce		Sputtering ion resource			Magnetron sputtering			The background vacuum Pressure (Pa)
plate voltage (keV)	beam current (mA)	plate voltage (keV)	beam current (mA)	Working Gas Pressure (Pa)	Power (W)	Working Gas Pressure (Pa)	Temperature on substrates (K)	
15-35	2	2.5	60	2.2×10^{-2}	200	1.1	Self-heating	5×10^{-4}

2.2. Evaluation

Hitachi S4800 scanning electron microscope was used to observe the morphology of the composites. The orientation of Ag films was characterized by D5000 X-rays diffraction (XRD) instrument, with a CuKa radiation source.

In the case of the silver-plated molybdenum foils, the adhesive strength P between films and substrate was expressed as

$$P=F/A \tag{1}$$

Where, ***A*** and ***F*** are the area of the flaking Ag thin films and the maximum force, respectively, when the Ag thin films had been pulled off from Mo substrate.

The electrical properties of the samples were tested by SB2232 DC digital resistance test instrument. By measuring the resistance ***R***, area ***A*** and thickness ***L*** of the samples, the electrical conductance $\boldsymbol{\kappa}$ can be calculated according to the equation (2).

$$\kappa = 1/\rho = \mathrm{L}/(R\cdot A) \tag{2}$$

3. Results and discussions

3.1. Orientation of the Ag thin films

The XRD spectra of the Ag thin films on Mo(200) substrate by different deposition methods was shown as figure 4. It can be seen from figure 4(a) that the Ag thin films deposited by MD method, exhibited (111) and (200) mixed orientation, while the (111) diffraction peak intensity was about two times than (200); When the films was deposited by IBD method, the (200) peak was greatly weakened and exhibited high preferred (111) orientation, and the (111) diffraction peak intensity was about five times than (200), as seen in figure 4(b). However, as seen in figure 4(c), when the Ag thin films deposited by IBAD method, its (200) peak was greatly enhanced and the (200) diffraction peak intensity was about ten times than (111) . And on this basis, the Mo substrate coated the Ag thin films by IBAD method, was deposited a layer of Ag thin films again by MD method. It could be found that the Ag thin films was showed a perfectly (200) preferred orientation, as shown in figure 4(d).

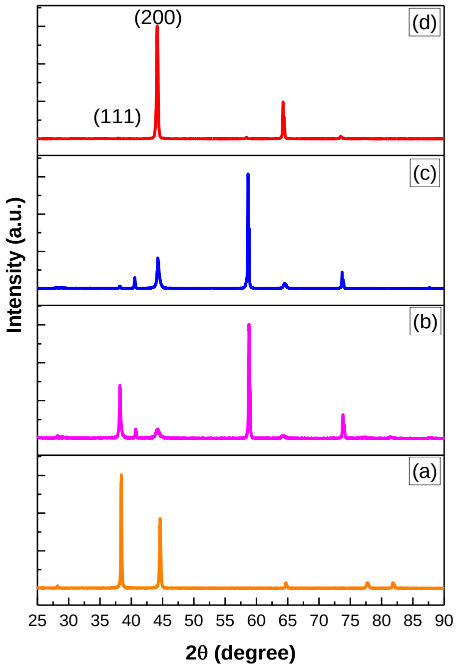

Figure 4. X-ray diffraction spectra of the Ag thin films on Mo(200) substrate (a) Deposited by MD(about 40 minutes), (b) Deposited by IBD(about 40 minutes), (c) Deposited by IBAD(about 40 minutes), (d) Deposited by MD(about 30 minutes) after IBAD(about 40 minutes).

The effect of IBAD on the preferred orientation of deposited films had been intensively studied[10-13]. In general, the prevailing model in which the texture transformation is attributed to a competition between anisotropic interface and strain energies, channeling effects, surface energy of the thin films, micro-structure and stresses of the substrate surface, and so on.

Usually, based on the thermodynamic stability theory, the thin films deposited by PVD (physical vapor deposition) grows with the plane of highest atomic density parallel to the substrate or the plane with minimum strain energy. For FCC (face-centered-cubic) materials such as Ag, its (111) crystal plane was the plane of highest atomic density as well as the lowest surface energy, so the thin films were highly preferred (111) orientation. Only if thought about surface energy, the preferred orientation were mainly (111) crystal planes, which had been reported for FCC metal films such as Au, Al, Ag, Cu and so on.

Compared to MD or IBD, the growing films were continuously bombarded by more high-energy Ar^+ ions with the assisted ion resource during IBAD. Namely, the energy of the ions was strong enough to clean the substrate's surface. Even if the assisted ion beam could induce atomic sputtering from surface, it could induce damage were significantly reduced when the ion beam was oriented along channeling directions of the films, which were named channeling effects. According to the study results about channeling effects[14-16], the sputtering yields in [111] direction is greater than that of in [100] direction in FCC materials. So, the growth speed of the films with (100) orientation was enhanced relatively, and the Ag films exhibited weak (111) and strong (200) mixed orientations. What is more, this layer of thin films would play an important role to induce the growth of the thin films deposited by MD along (200) orientation. Finally, the Ag thin films showed a perfectly (200) preferred orientation. Therefore, in the process of IBAD, the role of the channeling effects was more important than surface energy .

3.2. The adhesive strength between films and substrate

For silver-plated molybdenum interconnection-materials, because of the difference of the CTE (coefficient of thermal expansion) between Ag and Mo (Ag $19.2\times10^{-6}K^{-1}$, Mo $5.4\times10^{-6}K^{-1}$), the higher thermal stress was produced at the interface between the Ag films and the Mo substrates. Therefore the interconnectors would be bent over, broken and even distorted, if this thermal stress was higher enough. Based on the previous study [17], the interconnectors with sandwich-structure formed by the Mo foils deposited Ag thin films two sides should been designed for reducing some thermal stress. The cross-section micro-graph of this kind of Ag/Mo/Ag composites was shown as figure 5. It can be seen that the Ag films had very uniform thickness, and the cohesion of films/substrate were ideal.

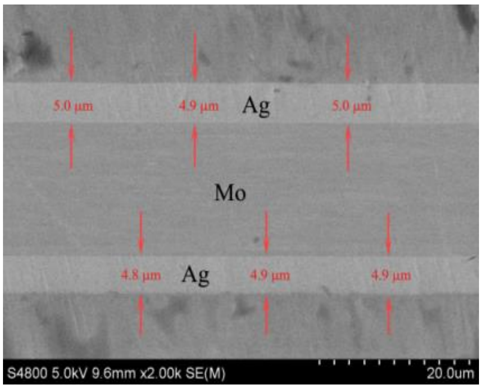

Figure 5. Cross sectional SEM image of the Ag/Mo/Ag composites made by MD after IBAD Ag thin films on the Mo foils.

The adhesive strength between the substrates and the films deposited by IBAD was significantly improved, which was attributed to the change of the interface bond model between the films and the substrate [18] mainly. It was found that the Ag thin films made by MD directly very easily desquamated from the substrates, because the combinative state between the films and the substrate could be physical mainly and the adhesive strength was lower. But during the IBAD process mentioned above, the growing film was continuously bombarded by a lots of high-energy Ar^+ ions, and a similar "ion implantation" effects was produced. So a part of Ag atoms could enter the Mo substrates to a depth of several nanometers from the surface, while a transition layer was made through the mixture of Ag and Mo atoms under the influence of ion beam. And the interficial combinative state between the films and the substrate was changed to metallurgical also. Moreover, the transition layer has a good thermal match with Ag or Mo because its CTE was between of them. The adhesive strength was significantly improved also. Moreover, the energy of ion beam had a profound impact on the adhesive strength during the IBAD process. The data including ion beam energy, the test results of the bond strength between the films and substrate, the area of the flaking Ag thin films and the maximum tensile force when the ion beam energy was changed, were given in table 2. Where, the interfacial adhesive strength was calculated by equation (1).

Table 2. Interfacial adhesive strength at different assisted ion beam energies

Samples' number	Assisted ion beam energy /keV	the area of the flaking Ag thin films /mm^2	Maximum tensile force /N	interfacial adhesive strength /MPa
1	15	10.22	58.8	5.75
2	20	9.72	63.7	6.55
3	25	9.87	121.03	12.26
4	30	9.23	171.5	18.58
5	35	11.21	117.6	10.49

According to the results of table 2, it can be found that the interfacial adhesive strength had been increased to 18.58MPa when the energy of ion beam was 30keV. With the increase of energy, the depth of bombardment and the thickness of the Ag-Mo mixed-layer were increased respectively. Therefore, the interfacial adhesion strength was increased with them. However, with the further increase of the ion beam's energies, the Ag particles entering the Mo substrate maybe too deep to form a effective transition layer on the substrate's surface, which made the interfacial adhesive strength decreased.

3.3. *Electrical properties*

The electrical performance of the silver-plated molybdenum composites was studied in this paper. The test results of the composites' electrical conductivity was shown as table 3. Where, the electrical donductivity of the composites was calculated by equation (2).

Table 3. Test results of electrical conductivity of composites

Thickness of the Mo foil / μm	Total thickness of Ag films both sides / μm	Resistance of the composites /mΩ	Electrical conductivity of the composites / $\times 10^6$S·m^{-1}
12	10	10.60	31.2
17	10	9.16	29.4

It can be seen that the increase of the electrical conductivity of composites along with the increases of Ag layer thickness ratio. So using the 12μm thick Mo foils, the current transmission loss would be reduced on some level. With 12μm thick Mo foil for example, according to the different current transmission modes in series or parallel, the calculated value of electrical conductivity of the composites was from 26.77×10^6S·m^{-1} to 38.51×10^6S·m^{-1}. And the test results was 31.2×10^6S·m^{-1}, which illustrated that the interfacial contact resistances were very small and further explained that the combination between the films and the substrate was very close.

4. Conclusions

For interconnected materials of solar cell array, compared to the pure silver foils or gold-plated silver foils, the silver-plated molybdenum composites have more excellent AO resistance performance. The preparation and performance of the silver-plated molybdenum composites was studied in this paper. It was found that the Ag thin films deposited by different preparation process showed different crystal orientation. Using of IBAD methods, the interfacial adhesive strength could been increased dramatically, and hence the electrical conductivity of the composites was more than 30×10^6S·m^{-1}. Which could meet the requirements of the longtime for the LEO spacecraft.

Acknowledgments

This work is supported by the National Natural Science Foundation of China under grant No. 51401080.

References

[1] S W Samwel 2014 Space Research Journal **7** p 1
[2] Dooling D and Finckenor MM 1999 NASA **TP-1999-209260** p 1
[3] LEE A and G Rhoads 1985 20th Thermophysics Conference p 1065
[4] M Raja Reddy 1995 Journal of Materials Science **30** p 281
[5] de Rooij A 2010 ESA/ESTEC EUROCORR (Moscow) p 1
[6] George C 1976 NASA-CR-**144312** p 1
[7] Silverman E M 1995 NASA-CR-**4661** p 1
[8] W Luft 1971 Transactions on aerospace and electronic systems p 781
[9] Yuan HUANG, De-yue KONG and Fang HE 2012 Acta metallurgica sinica **48** p 1253
[10] Jian-min ZHANG and Ke-wei XU 2003 ACTA PHYSICA SINICA **52** p 145
[11] Tao FENG and Bing-yao JIANG et al. 2008 Applied Surface Science **254** p 1565

IOP Conf. Series: Materials Science and Engineering **229** (2017) 012010 doi:10.1088/1757-899X/229/1/012010

[12] Huan Ma and Yu Zou Alla et al. 2015 Acta Materialia **98** p 17
[13] V A Gasparov and M Riehl-Chudoba 2007 Surface Science **601** p 5403
[14] Lindhard J 1965 Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd **34** p 64
[15] J W Mayer and E Rimini 1977 *Ion Beam Handbook for Material Analysis*(New York: Academic Press) p 67
[16] Matteo Seita and Christina M Pecnik et al. 2010 Acta Materialia **58** p 6513
[17] Pei QIU and Jia-jun ZHU 2015 Materials Review **29** p 143
[18] Ling-ping ZHOU and Ming-pu WANG et al. 2008 Transactions of Nonferrous Metals Society of China **18** p 372