Science Press

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Trans. Nonferrous Met. Soc. China 18(2008) 372−377

Transactions of Nonferrous Metals Society of China

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Enhanced adhesion of Cu-W thin films by ion beam assisting bombardment implanting

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Received 6 September 2007; accepted 19 November 2007

Abstract: Cu-W thin film with high W content was deposited by dual-target DC-magnetron co-sputtering technology. Effects of the substrates surface treating technique on the adhesive strength of Cu-W thin films were studied. It is found that the technique of ion beam assisting bombardment implanting of W particles can remarkably improve the adhesive property of Cu-W thin films. Indentation and scratching test show that, the critical load is doubled over than the sample only sputter-cleaned by ion beam. The enhancing mechanism of ion beam assisting bombardment implanting of Cu-W thin films was analyzed. With the help of mid-energy Ar^+ ion beam, W atoms can diffuse into the Fe-substrate surface layer; Fe atoms in the substrate surface layer and W atoms interlace with one another; and microcosmic mechanical meshing and diffusing combination on atom-scale among the Fe and W atoms through the film/substrate interface can be formed. The wettability and thermal expansion properties of the W atoms diffusion zone containing plentiful W atoms are close to those of pure W or W-based Cu-W film.

Key words: Cu-W thin film; adhesive strength; ion beam; magnetron sputtering; interface

1 Introduction

Cu-W film is a new functional material. There are Cu-based soft films and W-based hard films. Prior studies on Cu-based soft films and multilayer films have identified microstructures and deposition techniques [1−5]. CHU et al[6] reported that the Cu-W films with 11.1% (mole fraction) of tungsten content were synthesized using RF magnetron sputtering deposition, and the presence of W appeared to play a significant role in improving hardness and wear resistance of films. In recent years, W-based hard film with high hardness, low expansion and good electrical conductivity is the most promising in electronic packaging and wear- or erosion-resistant components usage[6−8]. However, poor adhesive strength of interface caused by poor wettability and the mismatch of crystal lattices and coefficient of thermal expansion between Cu-W thin film of W-based and metal substrates is serious problem for its practical use. So, how to improve the adhesive strength of Cu-W thin film becomes important and attractive. The adhesive property of thin film is controlled by various factors, such as the surface state of the substrate, the interior stress of thin film, the process of thin film deposition and the combination mode of the interface between thin film and the substrate[9−10]. The combined form of thin film and the substrate is the most key factor to determine the adhesive property of thin film. The combined form of thin film is often controlled by interlayer technology, the interface reaction and the interface diffusion[10−12]. In this work, ion beam assisting deposition(IBAD) and magnetron sputtering deposition were combined to prepare W-based Cu-W thin films to enhance adhesive property of Cu-W thin film.

2 Experimental

Cu-W thin films were deposited by dual-target DC-magnetron co-sputtering technology in MIS800 multi-function device with ion beam sputtering and magnetic

Foundation item: Project(05JJ3005) supported by the Natural Science Foundation of Hunan Province, China
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sputtering. These two targets were 99.95% pure tungsten and 99.99% pure copper. The working gas was 99.99% pure argon. A base vacuum pressure was 5×10^{-4} Pa and the working pressure was 1.0 Pa. The distance from substrate to target was fixed at 9.0 cm.

The substrate was $45^{\#}$ quenched steel (HRC$\geqslant$50) and its surface was ultrasonic cleaned in acetone and ethanol bath. Prior to deposition, the surface of the substrates was treated by the techniques shown in Table 1. The technique of ion beam assisting bombardment implanting of W particles in Table 1 includes four processes, and the total time of the processes is 40 min, which are shown in Table 2. The composition of Cu-W thin film was controlled by sputtering power of the two targets. The substrate holder was rotated and cooled by 20 ℃ water while films were deposited.

The composition of Cu-W thin film was determined by X-ray energy dispersive spectrometer(EDS) (Oxford Inca). The surface morphology was observed by a field emission scanning electron microscope(SEM) (JSM-6700F). The crystalline structure was analyzed by X-ray diffractometry(XRD) (Siemens D-5000). W atoms distribution with the depth of substrate surface layer was analyzed by AES (PHI-700). The micro-hardness was measured by MM6 metallographic microscope with micro-hardness annex. The adhesive strength was determined by indentation and scratching method.

3 Results and discussion

Fig.1 shows the composition and the structure of as-deposited Cu-W thin film. The result of EDS reveals that the film is $Cu_{34}W_{66}$, which belongs to W-based Cu-W thin film. The results of XRD show that only bcc diffraction peaks similar to W appear and no fcc diffraction peaks similar to Cu appear. The diffraction peaks are found to shift to the higher angle side compared with that of pure W, which indicates that metastable solid solutions of W-based Cu-W thin film are formed. The micro-hardness(HV) of the film approaches

Table 1 Treatment technique of substrates surface

Technique No.	Technique	Method	Remark
1	No treatment	Substrate surface was not sputter-cleaned by ion beam.	
2	Ion beam sputter-cleaning	Substrate surface was sputter-cleaned by ion beam with 500−800 eV and 30−60 mA.	
3	Ion beam assisting bombardment implanting of W particles	W film was sputter-deposited by ion beam with 2.5 keV and 60/10 mA and bombarded by another ion beam with 25 keV and 2/6 mA synchronously. The beam-currents of sputtering ion beam and bombardment ion beam were alternated every 10 min.	Substrate surface was sputter-cleaned by ion beam with 500−800 eV and 30−60 mA before these techniques.
4		W film was sputter-deposited by ion beam with 2.5 keV and 60/10 mA and bombarded by another ion beam with 30 keV and 2/6 mA synchronously. Beam-currents of sputtering ion beam and bombardment ion beam were alternated every 10 min.	
5		W film was sputter-deposited by ion beam with 25 keV and 60 mA and bombarded by another ion beam with 30 keV and 6 mA synchronously. The beam-currents of sputtering ion beam and bombardment ion beam were fixed.	

Table 2 Process of ion beam assisting bombardment implanting of W particle

Process	Time/min	Technique 4 (30 keV, alternative)			Technique 5 (30 keV, fixing)		
		Bombardment ion beam current/mA	Sputtering ion beam		Bombardment ion beam current /mA	Sputtering ion beam	
			Energy/keV	Beam current/mA		Energy/keV	Beam current/mA
1	10	2	2.5	60	6	2.5	60
2	10	6	2.5	10	6	2.5	60
3	10	2	2.5	60	6	2.5	60
4	10	6	2.5	10	6	2.5	60

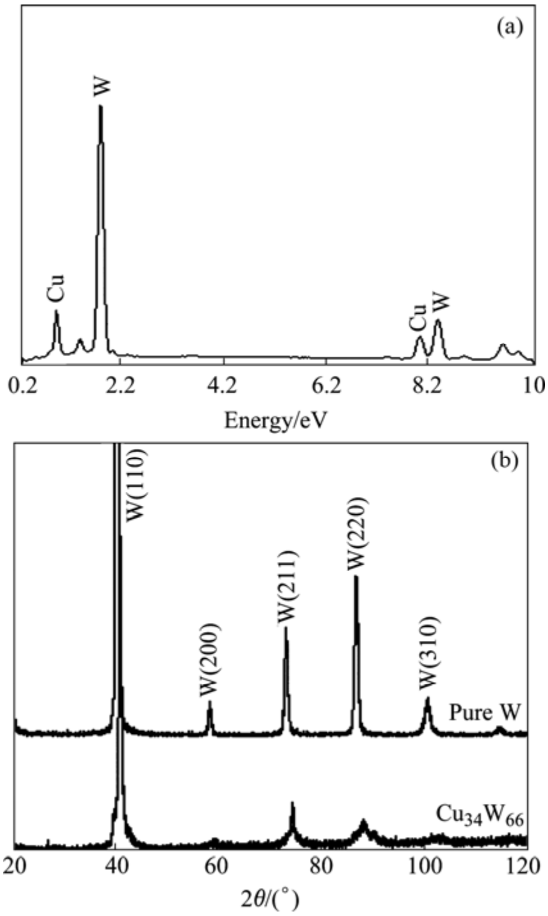

Fig.1 EDS pattern (a) and XRD patterns (b) of Cu-W thin film

1.343 GPa. The metallic wettability of these films is as poor as that of pure W. So the films have poor strength adhesion to the substrate, and the thin films deposited directly will generally delaminate automatically.

Fig.2 shows indentation critical load of Cu-W thin films deposited on the different surfaces of substrates treated by the techniques in Table 1. The larger the indentation critical load, the higher the adhesive strength of thin films[13]. The adhesive property of as-deposited films is obviously improved by ion beam assisting bombardment implanting of W particles. The adhesive strength of Cu-W thin films can be further increased by alternating beam current of sputtering and bombardment ion.

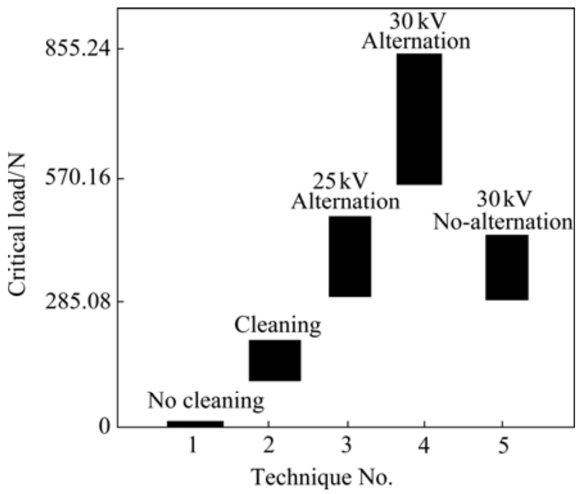

Fig.2 Adhesive property of Cu-W thin film deposited on different treating surfaces of substrates

In indentation test, a static stress load is applied on the Cu-W thin films, and the thin films gradually split and desquamate with increasing the pressure. Fig.3 shows indentation morphologies of the Cu-W thin film deposited on the substrate surface only sputter-cleaned by ion beam (Technique 2 in Table 1) at various loads. The thin film does not desquamate at the small load, as shown in Fig.3(a). The small pieces of thin films begin to desquamate when the load reaches a certain degree, as shown in Fig.3(b), which is regarded as the critical load. With the load further increasing, the desquamating area increases, as shown in Figs.3(c) and (d).

Fig.4 shows indentation morphologies of the Cu-W thin films deposited on the substrate surface modified by the technique of ion beam assisting bombardment implanting W particles at various loads. With the load increasing, the indentation diameter increases, and the film does not desquamate obviously in large area. When the load approaches 470 N, the small pieces of thin films surrounding indentation trail zone begin desquamating, and the desquamating degree of the thin film almost remains unchanged with the load further increasing. Comparing Fig.3(d) that is taken by technique 2 at the load of 313.6 N with Fig.4(a) that is taken by technique 4 at the load of 313.6 N, we can find that the adhesive property of Cu-W thin films deposited on the substrates surface modified by technique 2 is obviously different from that by technique 4. At the same load, Cu-W thin films deposited on the substrate only sputter-cleaned by ion beam (Technique 2 in Table 1) desquamate badly, however the thin films deposited on the substrate modified by ion beam assisting bombardment implanting W particles (Technique 4 in Table 1) desquamate scarcely. Therefore, the adhesive property of Cu-W thin film can be effectively enhanced by the technique of ion beam assisting bombardment implanting W particle into the substrate surface layer.

It can be seen from Fig.2, the adhesive strength of Cu-W thin films is very poor if the substrates are not sputter-cleaned by ion beam. Actually, the thin film desquamates soon after the sample is taken out from vacuum, which is attributed to existing of oxide films on substrate surface and other adsorbent, though substrate surface has been cleaned ultrasonically in the solution of acetone and ethanol, and these impurity remained at the interface between the film and the substrate causes the

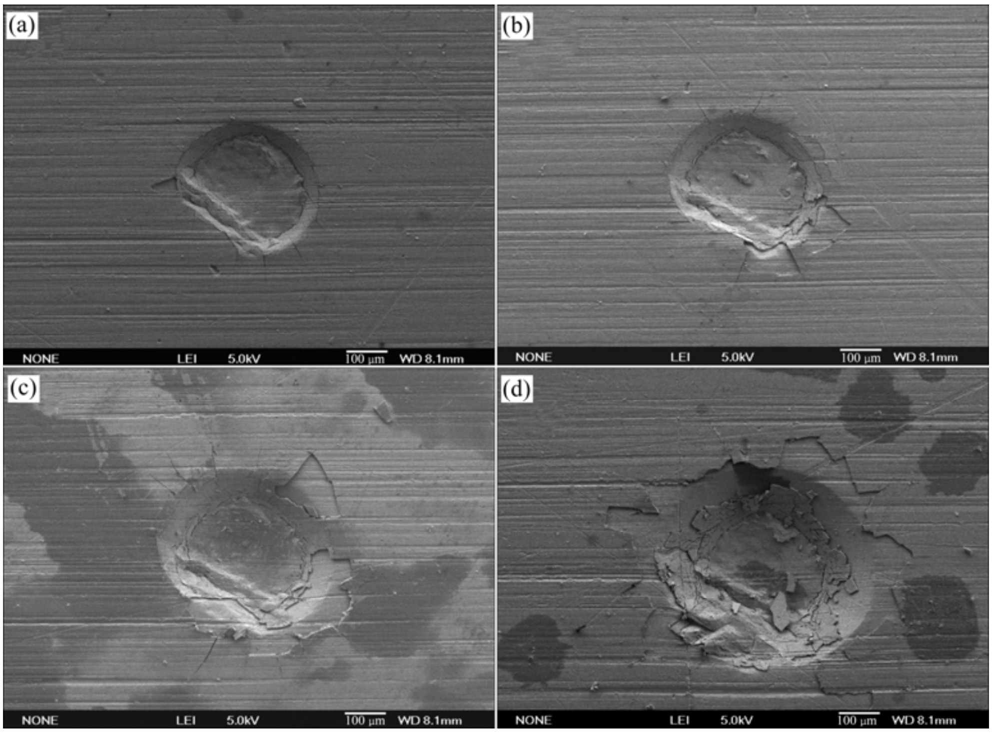

Fig.3 Indentation morphologies of Cu-W thin films deposited on substrate surface only sputter-cleaned by ion beam (Technique 2) under different static pressure loads: (a) 109.76 N; (b) 141.12 N; (c) 196.00 N; (d) 313.60 N

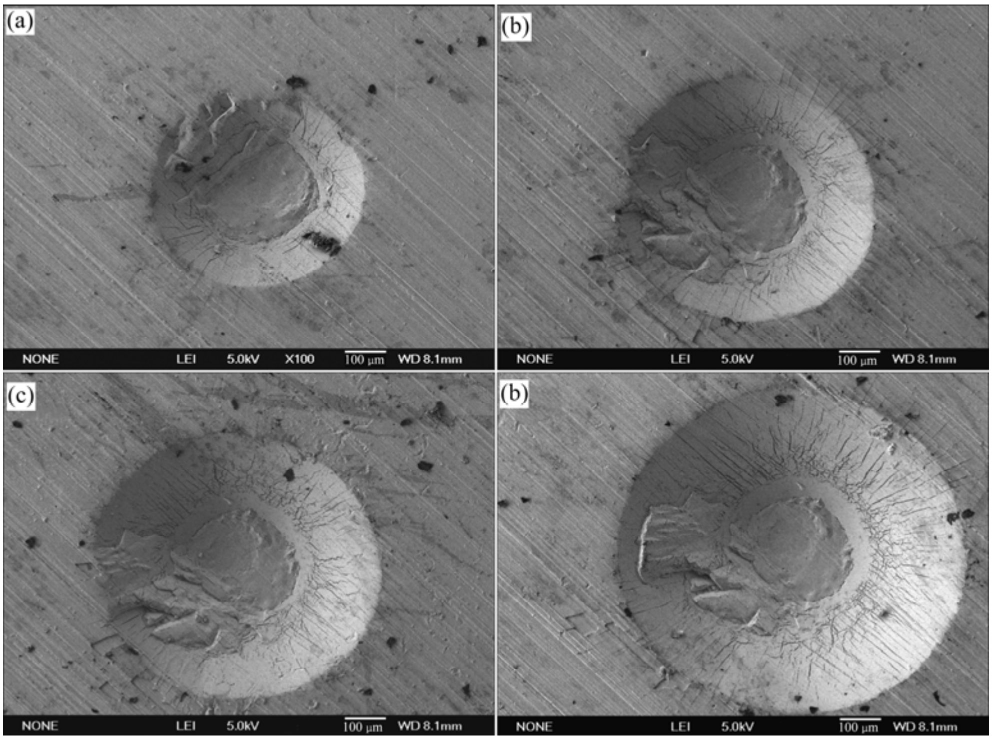

Fig.4 Indentation morphologies of Cu-W thin films deposited on substrate surface modified by ion beam assisting bombardment implanting W particles (Technique 4) under different static pressure loads: (a) 313.6 N; (b) 470.4 N; (c) 588.0 N; (d) 862.4 N

adverse effect on the adhesive property of Cu-W thin film. The oxide films and other adsorbent on the surface of substrate can be removed by ion beam sputter-cleaning, and fresh surface can be gained[14], which can improve the adhesive property of Cu-W thin film. However, the adhesive property of Cu-W thin film prepared by technique 2 is lower that of the sample prepared by techniques 3, 4 and 5. The energy of sputtering atoms from the target is so low that they are not implanted and diffused into the substrate surface layer when the temperature of the substrate maintains lower than 373 K by cooling water. They only accumulate to form thin film. The composition through the interface between Cu-W thin film and the substrate is discontinuous, which causes the interfacial stress to concentrate within 1-2 atoms layers and the stress to gradient is great, so the adhesive property of the film is not very good.

The influence of the substrate treatment technique on the adhesive property of Cu-W thin film is measured by scratching test at dynamic load, which corresponds to that at static load. Fig.5 shows scratching curves of the Cu-W thin films deposited on substrate surface modified by different techniques. During scratching test, the load applied on thin films increases continuously till the film crack forms. The transmitting voice signal exits, and the load is called as the critical load. The critical load is regarded as adhesive property of the film[15]. It can be seen from Fig.5 that the scratching critical load of the Cu-W thin films deposited on substrates modified by ion beam assisting bombardment implanting W particles is about two times larger than that only sputter-cleaned by ion beam.

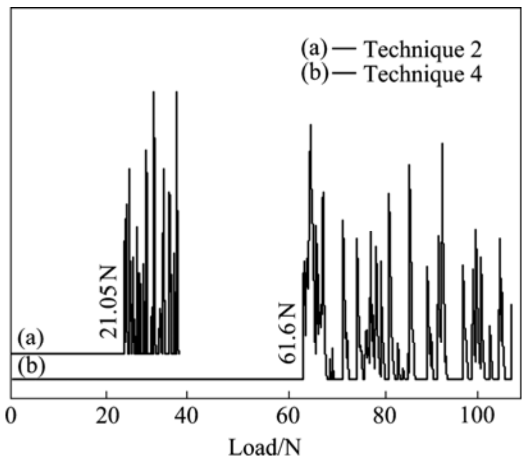

Fig.5 Scratching curves of Cu-W thin films

The technique of ion beam assisting bombardment implanting W particles can apparently improve the adhesive property of Cu-W thin films, which attributes to the change of the interface combining form between thin film and the substrate. Usually, film/substrate interface is combined by fine-mechanical mesh that is the process of indention interlocking between micron-scale notch and convex on the substrate surface and thin film. There is relationship between the fastness of indention interlocking and activity of sputter atoms. The activated atoms have excellent ability to fill notch. If activity of sputter atom is weak, it is easy to form the pinhole in the films, and the adhesive property of thin film is weakened. Moreover, because of different thermal expansion coefficient between thin film and the substrate, the mechanical meshing could be wrecked by heating. Ion beam assisting bombardment implanting W particles is the process that the atoms sputtered from the target can be implanted into a definite depth of the substrate surface layer by the help of mid-energy Ar^+ ion beam, as shown in Fig.6. With the help of mid-energy Ar^+ ion beam, W atoms can diffuse in the substrate surface layer. Fe atoms in the substrate surface layer and W atoms interlace with one another; and microcosmic mechanical meshing and diffusing combination on atom-scale among the Fe and W atoms through the film-substrate interface can be formed. The thermal expansion properties of this layer that contains plentiful W atoms will be close to those of pure W or W-based Cu-W film. Cu-W thin film with high W content is a W-based metastable solid solution, which has good wettability and interface matching with W. Cu-W thin film is in situ deposited prior to the substrate surface modified by ion beam assisting bombardment implanting W particles, which can help to overcome the problems of interface unmatched and the impurity such as oxygen invaded to interface. Therefore, the process of ion beam assisting bombardment implanting W particles can remarkably improve the adhesive property of Cu-W thin films.

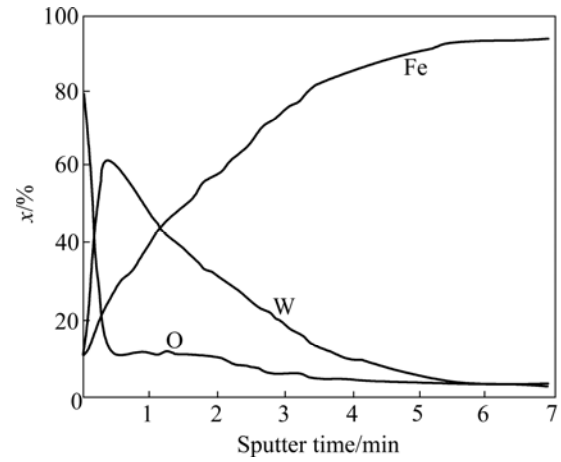

Fig.6 AES analysis of substrate surface modified by ion beam assisting bombardment implanting W particles

4 Conclusions

1) The technique of ion beam assisting bombardment implanting W particles can remarkably improve the adhesive property of Cu-W thin films. Indentation and scratching test show that, the critical loads approach 470 N and 61 N respectively, which is doubled over than the sample only sputter-cleaned by ion beam.

2) Cu-W thin film is in situ deposited prior to the substrate surface modified by ion beam sputter-cleaning

and assisting bombardment implanting W particles, which can help to overcome the problem of interface unmatched and the impurity such as oxygen, can not invade. With the help of mid-energy Ar^+ ion beam, W atoms can diffuse into the Fe-substrate surface layer; Fe atoms in the substrate surface layer and W atoms interlace with one another; and microcosmic mechanical meshing and diffusing combination on atom-scale among the Fe and W atoms through the film-substrate interface can be formed. The wettability and thermal expansion properties of the W atoms diffusion zone contained plentiful W atoms are close to those of pure W or W-based Cu-W film.

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(Edited by LI Xiang-qun)