Effects of annealing time on the structure, morphology, and stress of gold–chromium bilayer film*

Hong Zhang(张洪)[1,2], Yun-Xia Jin(晋云霞)[2,†], Hu Wang(王虎)[1,2], Fang-Yu Kong(孔钒宇)[2], Hao-Peng Huang(黄昊鹏)[1,2], and Yun Cui(崔云)[2]

[1] *University of Chinese Academy of Sciences, Beijing* 100049, *China*
[2] *Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Shanghai* 201800, *China*

(Received 10 March 2016; revised manuscript received 3 May 2016; published online 25 August 2016)

In this work, a 200-nm-thick gold film with a 10-nm-thick chromium layer used as an adhesive layer is fabricated on fused silica by the electron beam evaporation method. The effects of annealing time at 300 °C on the structure, morphology and stress of the film are studied. We find that chromium could diffuse to the surface of the film by formatting a solid solution with gold during annealing. Meanwhile, chromium is oxidized on the surface and diffused downward along the grain grooves in the gold film. The various operant mechanisms that change the residual stresses of gold films for different annealing times are discussed.

Keywords: gold–chromium film, film stress, diffusion

PACS: 42.79.Wc, 68.35.Gy, 68.35.Fx, 42.70.Hj **DOI:** 10.1088/1674-1056/25/10/104205

1. Introduction

Gold (Au) is a precious metal material, with excellent electrical, optical and mechanical properties. Au films have been used in diverse fields such as the sensor,[1] surface enhanced Raman spectroscopy,[2,3] nonlinear laser,[4,5] and photonic crystal.[6] Our previous work showed that Au film combined with dielectric multilayer films can be used to produce metal multilayer dielectric gratings (MMDG) for pulse compression.[7,8] Au film was used to provide a broad reflection bandwidth and reduce the number of dielectric multilayer films.[9,10] Dielectric layers are used to enhance laser damage resistance of the pulse compression gratings.[11] A thin chromium layer was deposited for adhering the Au film and substrate. During the fabrication of MMDG, a variety of organic and inorganic contaminants may be introduced into the grating grooves.[12] The cleanliness of the grating surface has an important influence on the diffraction efficiency and damage resistance of gratings used in the chirped pulse amplification systems.[13–15] However, the cleaning process itself would introduce the chemical degradation and thermal stresses in the coating, which leads to delamination and defects.[16,17] Gold–chromium bilayer is also used on the microcircuit that has been deposited on an alumina substrate. It was comprised of a thin chromium layer for adherence and a gold layer for conductance.[18] During annealing, the structure and composition of the film and interfaces were changed by the diffusion and segregation process.[19] Numerous studies focused on the diffusion processes and were concerned more about composition, structure and electrical properties of the films. Besides, the effects of diffusion on interfacial fracture of gold–chromium hybrid microcircuit films were investigated. Moody *et al.* demonstrated that chromium in solution is as effective as continuous chromium adhesive layers in promoting adhesion.[20]

However, the effect of annealing time on the film stress evolution has not been reported in detail. It is very significant for engineering such as metal multilayer dielectric grating. It is important to investigate the stress distribution and origin of the film. Previously, many studies were devoted to the origins and evolutions of polycrystalline films such as metal films grown through the Volmer–Weber mechanism. It is generally received that the tensile stress results from elastic strain associated with grain boundary formation during island coalescence.[21] Chason *et al.* argued that the compressive stress resulted from surface downhill currents which caused an excess of adatoms to be inserted into the grain boundaries (GBs).[22] Other models pointed out that the difference of the surface defect densities on the growth surfaces[23] and surface restructuring during growth interruption[24] could change the stress distribution in film. In this article, we investigate the effects of annealing time on the evolution of structural, morphological, and stress properties. It is found that the annealing time changes the distribution of chromium (Cr) in the gold film and has significant influences on the structural, morphological, and stress properties of the bilayer film.

*Project supported by the National Natural Science Foundation of China (Grant No. 61405225).
†Corresponding author. E-mail: yxjin@siom.ac.cn
© 2016 Chinese Physical Society and IOP Publishing Ltd

2. Experiments

The Au film in this study was deposited on fused silica (50 mm×5 mm×1.5 mm) by the electron beam evaporation method. Prior to deposition, the substrate was cleaned with petroleum ether and deionized water and then heated to 200 °C. Firstly, the Cr film about 10 nm was deposited on the fused silica at a vacuum pressure of 4.5×10^{-3} Pa to enhance the adhesion between substrate and gold film. Au film about 200 nm was deposited using the intrinsic Au target (purity 99.999%) at the same pressure and temperature with the evaporation voltage about 20 V and current about 200 A. The cavity naturally cooled to room temperature. Then the sample was transferred to the furnace for the annealing process. The temperature in the furnace was controlled from room temperature to 300 °C at a rate of about 4.4 °C/min in an atmospheric environment. In order to investigate the effects of annealing time on the structure, morphology, and stress of gold–chromium bilayer film, we fabricated five samples at the same time by the electron beam evaporation method and the samples were placed on the line adjacently to ensure the same property before annealing. The holding times were set to be 1, 3, 5, 7, and 9 h. The samples were then cooled to room temperature naturally.

The structural characteristics of the samples were examined by x-ray diffraction (XRD) using an x-ray diffractometer (Empyrean, PANalytical) with 2θ in a range of 10°–90° using Cu Kα radiation. The residual stress in the film was also determined by XRD measurement. This was accomplished by scanning the diffracted intensity at the diffraction angle (2θ) around the maximum of the selected peak, centered at (θ_{hkl}, $2\theta_{hkl}$). Each peak was scanned carefully in steps of 0.05°. The calculated stress results were given by the software (X'Pert Stress, PANalytical). Surface morphology and roughness were analyzed by atomic force microscopy (AFM, Dimension 3100, Bruker Nano Inc) by using the taping mode and scanning electron microscope (SEM, Auriga, Carl Zeiss). X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific) was used to identify the valence state and content of the elements in the film surface. Transmission electron microscopy (TEM) measurements were conducted with a (Tecnai G2 F20, FEI) microscope operating at 200 kV after samples had been prepared by focused ion beam milling. All measurements were performed at room temperature.

3. Results

Figure 1(a) shows the XRD patterns of the samples for different annealing times. There are four peaks and no other peaks exist despite different annealing times, which means that there exists only one phase in the film. These diffraction peaks are of Au crystal and no chromium is found. The strongest diffraction peak is located around 64.6° corresponding to the (220) lattice plane. Figure 1(b) gives the detailed 2θ degree of the (220) lattice plane and the corresponding interplanar spacing with different annealing times. The interplanar spacing decreases with the annealed time increasing from 1 h to 5 h and increases with prolonging the annealed time. Figure 1(c) gives the variations of full width at half maximum (FWHM) with annealing time for different samples. The FWHM has an opposite trend to the interplanar spacing. The FWHM increases from 1 h to 5 h, but declines from 5 h to 9 h. The variations of the interplanar spacing and FWHM can be attributed to other atoms occupying the positions of gold atoms. Meanwhile this process affects the crystallization quality of gold film.

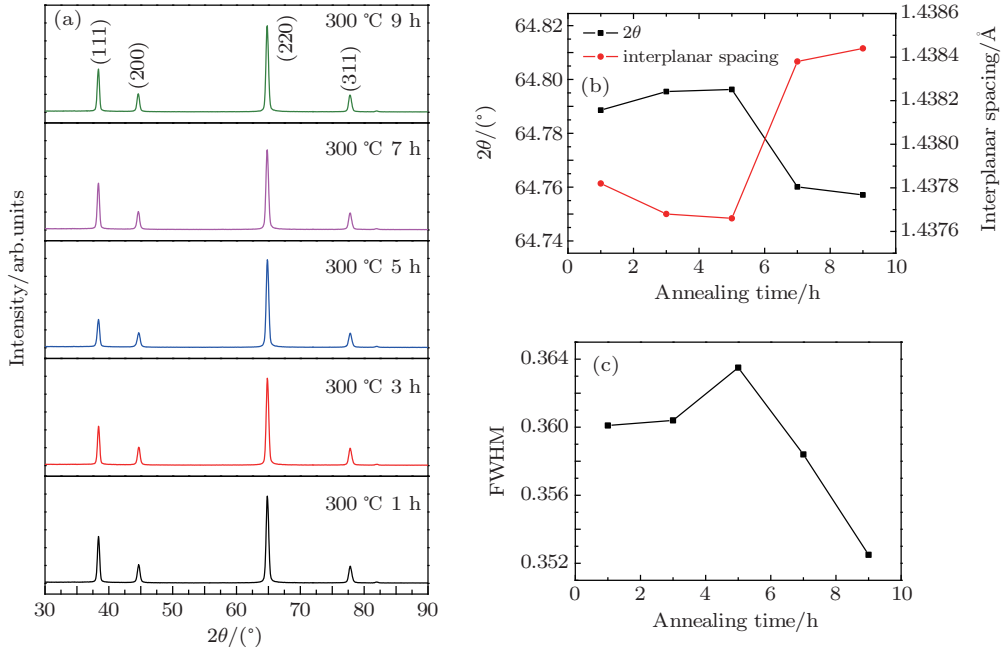


Fig. 1. (color online) (a) X-ray diffraction patterns, (b) 2θ of (220) lattice plane and, (c) FWHM of Au films for different annealing times.

Figure 2 shows the SEM images of the as-deposited sample and the samples with different annealing times. We take the images from the same positions of the samples. It is clear that some other substances that look like "white fleck" come out on the surface of the Au film just for an annealing time of 1 h. As the annealed time extends to 5 h, more white flecks come out and these white flecks become larger, which look like "islands floating in the sea". When the annealing time extends to 9 h, these white flecks tend to shrink and reduce. Relating them to the XRD patterns shows that these substances change the surface morphology of the Au film and partly affect the crystallizations of Au films. But we need XPS tests to determine the compositions of these substances. It is noticeable that grain boundary grooves and separation become clear when the samples are annealed for 7h and 9 h,[25] which suggests that the gold films are undergoing grain growth/consolidation.

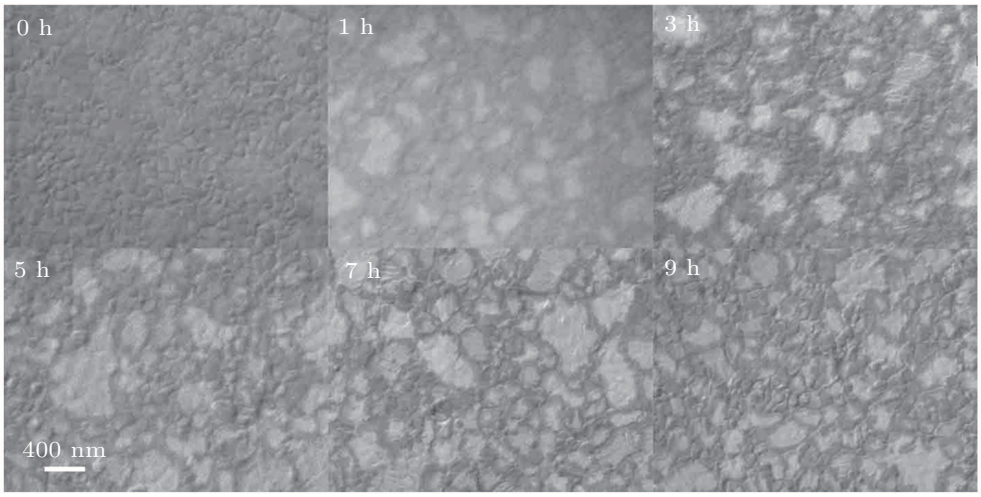


Fig. 2. SEM images for different annealing times.

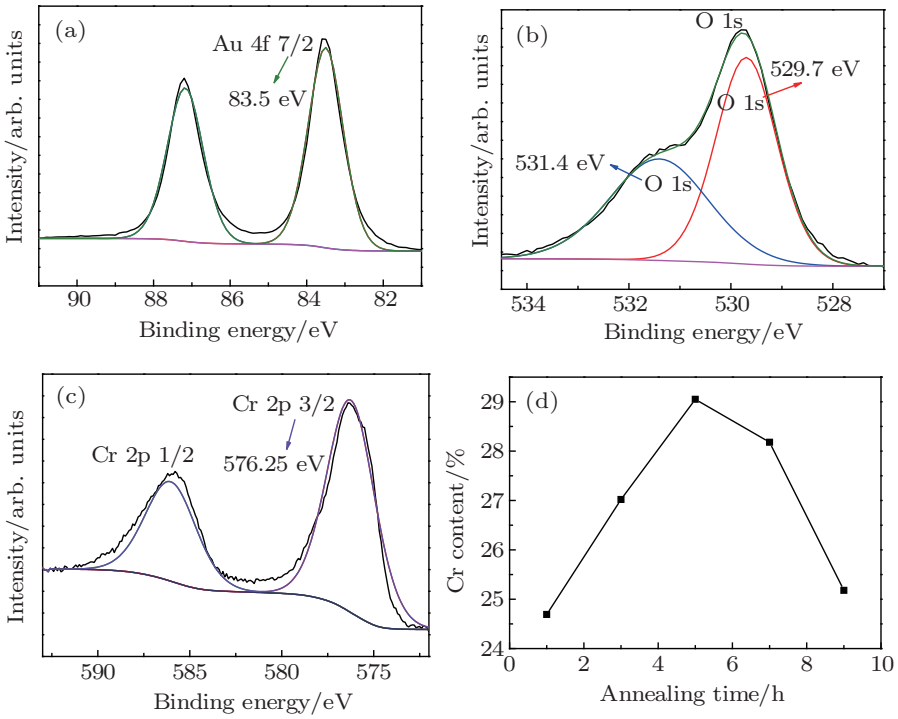


Fig. 3. (color online) XPS spectra of Au 4f (a), O 1s (b), and Cr 2p (c) of the sample with a 9-h annealing time. (d) Cr content on the surface of samples versus annealing time.

XPS could be used to determine the elements in the shallow surface about 10 nm in depth. We measured the Cr 2p, Au 4f, and O 1s XPS spectra of samples at different annealing times. In Table 1 we summarize the data of the binding energy of Cr 2p, Au 4f, and O 1s at different annealing times. All of the data are calibrated by using the reference da-

tum of C 1s = 284.6 eV. As for the data that change little from 1 h to 9 h, we just figure one example and discussed it. Figure 3(a) shows the Au 4f spectra of the 9-h annealed sample, the peak at BE = 83.5 eV is close to the reference datum of Au 4f(7/2) = 84 eV.[26] It suggests that the Au is still Au^0 metallic at different annealing times. Figure 3(b) shows the spectrum of O 1s. The O 1s spectrum is deconvoluted into two components at 531.4 eV and 529.7 eV. The peak at 531.4 eV is assigned to the organic compound and the peak at 529.7 eV is attributed to Cr_2O_3.[27] It is suggested that oxidation takes place and one kind of metallic oxide is generated. Besides, chromium is an oxygen-active material.[28] With the chromium content diffusing to the surface, the oxidation process happens rapidly in the air annealing. Figure 3(c) shows the Cr 2p spectrum. The peak at 576.25 eV is attributed to the Cr^{3+}.[29] It confirms that Cr comes onto the surface of the Au film and is oxidized. Besides, the peak at band energy of 574 eV–574.2 eV is an indication of metallic Cr^0.[30] But we do not find this peak in our study. It suggests that chromium is oxidized completely and only Cr_2O_3 is obtained on the surface. Figure 3(d) gives the variation of Cr content on the surface with the annealing time. Cr content reaches a value between 20% and 30% after annealing and increases from 1 h to 5 h and decreases from 5 h to 9 h. Relating this phenomenon to the images of morphology and structure, it can be deduced that the progress of Cr diffusion has important effects on the modification of the structure and morphology of the Au film.

Table 1. XPS data of Au 4f, O 1s, and Cr 2p for different annealing times.

	1 h/eV	3 h/eV	5 h/eV	7 h/eV	9 h/eV
Au 4f 7/2	83.52	83.47	83.54	83.59	83.5
O 1s (I)	531.47	531.52	531.49	531.46	531.44
O 1s (II)	529.85	529.89	529.78	529.78	529.7
Cr 2p 3/2	576.27	576.32	576.27	576.28	576.25
Cr 2p 1/2	586.05	586.1	586.05	586.09	586.03

We care more about the variations of residual stress in Au films with different annealing times. Figure 4 presents residual stress versus annealing time. All the samples exhibit a tensile stress and have an order of magnitude of 10^2 MPa each. When annealing time increases from 1 h to 5 h, the residual stress in each of the films increases. When annealing time increases to 9 h, the residual stress decreases significantly. We prove that there appear Cr atoms on the surface of film after annealing. Besides, it is interesting to note that the residual stress changes in a similar trend to the Cr content change in Fig. 3(d). We try to find the way Cr atoms diffuse to the surface and the relationship between diffusion and residual stress.

Microstructures of the as-deposited sample and the 5-h annealing sample are characterized by transmission electron microscopy (TEM). Figure 5 shows the cross-sectional bright field TEM images of samples. From Figs. 5(a) and 5(c), we can see that the samples are polycrystalline thin films no matter whether they are annealed. There are a lot of grain boundaries in the Au film and they construct channels between the top and bottom of Au film. By comparing Fig. 5(b) with Fig. 5(d), the thin chromium layer is continuous before annealing. After annealing, the chromium layer at the bottom is interrupted but crystallizes better. As shown in Fig. 5(e), several layers of chromic oxide cover some areas of the surface of the gold film after annealing for 5 h. Meanwhile, figure 5(b) shows that numerous stacking faults, dislocations, and some twins are evident in the gold films but significantly reduce after annealing (Fig. 5(d)). This reduction is attributed to the chromium diffusion process and grain growth. For the annealing sample, we use the EDS spectrum through the grain boundary between two grains to identify whether chromium atoms diffuse through the grain boundary. The result in Fig. 5(f) shows that the chromium atoms exist in both grain interior and grain boundary and the chromium content in the grain boundary is not much higher than that in the internal grain, which is not consistent with the result in the literature.[22] Therefore, we believe that the grain boundary is not the only way chromium diffuses to the top surface. The authors hold the perspective that metal atoms migrate through the grain boundary in the vacuum coating. This may be because the diffusion process of chromium does not have high mobility compared with that deposited in a vacuum coater. According to the Au–Cr phase diagram, chromium solubility in gold may be about 20% at 300 °C. In our work, when the annealing temperature rises, chromium atoms diffuse into the gold grains; and when the temperature drops, some of the chromium atoms migrate to the surface of the film and are oxidized. This process is coincident with that indicated by XRD results.

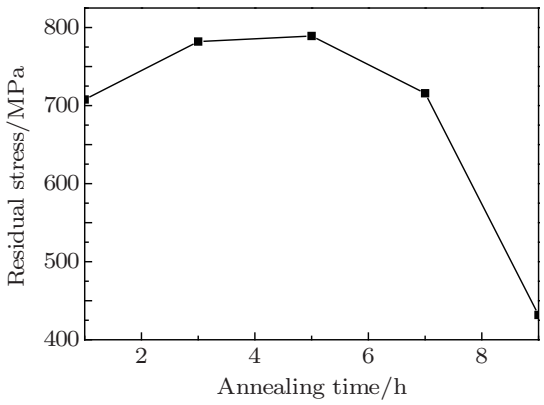


Fig. 4. Residual stress versus annealing time for sample.

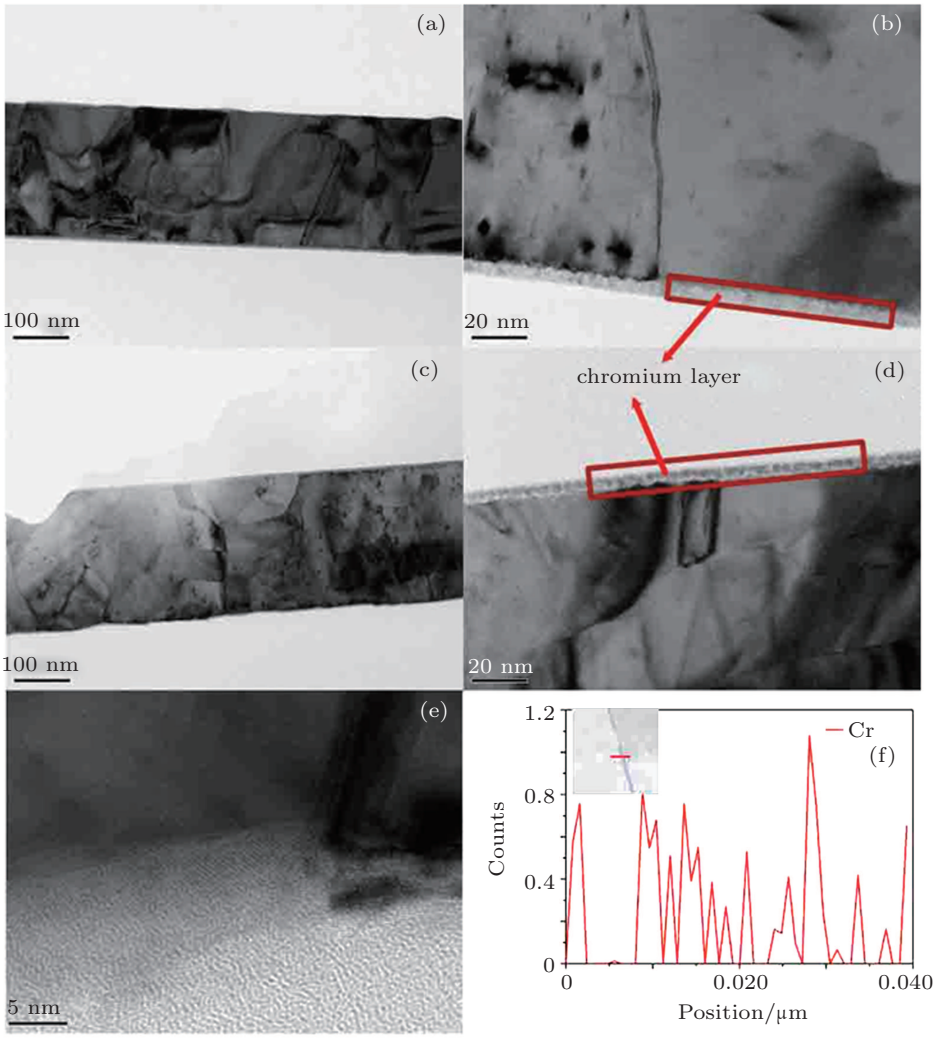


Fig. 5. (color online) Cross-sectional bright field TEM images of Au films (a) and (b) for as-deposited, (c)–(e) for 5-h annealing, (f) the variation of Cr content through the grain boundary between two grains.

4. Discussion

Correlating what we have found above, we can understand the diffusion process varying with the annealing time and its effects on the structure, morphology and residual stress of gold film. When the samples are annealed for 1 h, the gold film experiences a grain growth process. At the same time, chromium atoms diffuse to gold film gradually. When the annealing time is extended to 5 h, more and more chromium atoms diffuse to gold films in two ways: one is to form a solid solution with gold and the other is to pass through the grain boundary. Besides, forming a solid solution is a dominant way of the diffusing process, which is proved by the results of XRD and TEM. The former way means that the chromium atom occupies the position of a gold atom in the lattice. The atomic volume of chromium is smaller than that of gold, so the interplanar spacing of (220) decreases. At the same time, the FWHM increases because of the lattice deformation. Generally, the residual stress in the metallic material is caused by volumetric change.[25] The subtraction of volume leads to the increase of tensile stress in the gold film.[31] When gold atoms are replaced by chromium atoms, the volume of unit cell shrinks. Besides the process including defect motion and consolidation, and grain growth, the hillock also subtracts the volume of film.[31] In our work, these processes lead to the tensile stress increasing in the gold film in Fig. 5. When the annealing time is prolonged to 9 h, some other processes happen. As for the residual stress, the process including precipitation,[32] grain boundary separation,[33] and grain boundary grooving[34] adds volume, thereby leading to the increase of compressive stress in the gold film. Additionally, chromium is an oxygen-active material. Chromium oxide is generated and accumulated with more chromium atoms diffusing to the surface. Then chromium oxides diffuse to the grain boundary grooves rather than form a solid solution with the gold again, which means that the mass transport happens on the surface. The spread direction of the chromium oxide is downward along the grain boundary. This process is volumetrically additive and speeds up the development of compressive stress in the gold film. Meanwhile, the process that chromium atoms diffusing to the surface through grain bound-

aries is disturbed. Besides, the chromium layer is interrupted but crystallized better. The diffusion velocity from chromium layer to gold layer slows down. However, more chromium atoms diffuse to the surface from the gold grain lattice and more chromium oxides diffuse to grooves. These processes play a dominant role so the residual stress tends to be compressive and the crystallization of gold film is better.

5. Conclusions and perspectives

Gold films are prepared by the electron beam evaporation method. The effects of annealing time on the structure, morphology, and residual stress of gold film are studied. It is found that the thin chromium layer used to enhance the adhesion at the bottom will diffuse to the surface of the film partially in the annealing process. When annealing time increases from 1 h to 5 h, the chromium atoms diffuse to the surface by forming a solid solution with gold mainly. The residual stress of the gold film tends to increase tensile stress. Chromium atoms replace gold atoms in the lattice, thereby leading to subtractive volume and reduced interplanar spacing. Both replacement and grain growth result in tensile stress. When annealing time extends to 9 h, residual stress develops in the direction of compressive stress. Grooves form and grow at the grain boundaries. Also, chromium oxide diffuses to the grooves and downward to the grain boundary. These processes explain the increased compressive stress for 5 h annealing. The various microstructure changes and operant mechanisms compete between each other, which results in a sophisticated phenomenon in the gold films. It is concluded that changing the annealing time is an effective method to adjust the residual stress in Au film. Our work shows a potential for avoiding the delamination of MMDG by optimizing the annealing process.

References

[1] Nakano N and Ogawa. S 1994 *Sensor Actiat B-Chem.* **21** 51

[2] Baia. M, Baia L and Astilean S 2005 *Chem. Phys. Lett.* **404** 3

[3] Zhong Y T, Cheng Z Q, Ma L, Wang J H, Hao Z H and Wang Q Q 2014 *Chin. Phys. Lett.* **31** 047302

[4] Xenogiannopoulou E, Iliopoulos K, Couris S, Karakouz T, Vaskevich A and Rubinstein I 2008 *Adv. Funct. Mater.* **18** 1281

[5] Hohenau A, Krenn J R, Garcia-Vidal F J, Rodrigo S G, Martin-Moreno L, Beermann J and Bozhevolnyi S I 2007 *Phys. Rev. B* **75** 085104

[6] Ding B, Pemble M E, Korovin A V, Peschel U and Romanov S G 2010 *Phys. Rev. B* **82** 035119

[7] Guan H Y, Chen H, Wu J B, Jin Y X, Kong F Y, Liu S J, Yi K and Shao J D 2014 *Opt. Lett.* **39** 170

[8] Guan H Y, Jin Y X, Liu S J, Kong F Y, Du Y, He K, Yi K and Shao J D 2014 *Appl. Phys. B* **114** 557

[9] Bonod. N and Neauport. J 2006 *Opt. Commun.* **260** 649

[10] Palmier S, Neauport J, Baclet N, Lavastre E and Dupuy G 2009 *Opt. Express* **17** 20430

[11] Liu S J, Ma J Y, Shen Z C, Kong W J, Shen J, Jin Y X, Zhao Y A, Shao J D and Fan Z X 2007 *Acta Phys. Sin.* **56** 4542 (in Chinese)

[12] Xu X D, Liu Y, Qiu K Q, Liu Z K, Hong Y L and Fu S J 2013 *Acta Phys. Sin.* **62** 234202 (in Chinese)

[13] Howard H P, Aiello A F, Dressler J G, Edwards N R and Kessler T J and Kozlov A A, Manwaring I R, Marshall K L, Oliver J B and Papernov S 2013 *Appl. Opt.* **52** 1682

[14] Chen, S B, Sheng B, Xu X D and Fu S J 2010 *Proc. SPIE* **7655** 22

[15] Ashe B, Giacofei C, Myhre G and Schmid A W 2007 *Proc. SPIE* **6720** 67200N

[16] Liddell H P, Mehrotra K, Lambropoulos J C and Jacobs S D 2013 *Appl. Opt.* **52** 7689

[17] Wu J B, Jin Y X, Guan H Y, Kong F Y, Liu W W, Liu S J and Yi K 2014 *J. Inorg. Mater.* **29** 1087

[18] Munitz A and Komem Y 1976 *Thin Solid Films* **37** 171

[19] George M, Glaunsinger W, Thundat T and Lindsay S 1990 *Thin Solid Films* **189** 59

[20] Moody N, Adams D, Medlin D, Headley T, Yang N and Volinsky A 2003 *Int. J. Fracture* **120** 407

[21] Nix W and Clemens B 1999 *J. Mater. Res.* **14** 3467

[22] Chason E, Sheldon B, Freund L, Floro J and Hearne S 2002 *Phys. Rev. Lett.* **88** 156103

[23] Friesen C and Thompson C 2004 *Phys. Rev. Lett.* **93** 056104

[24] Koch R, Hu D and Das A 2005 *Phys. Rev. Lett.* **94** 146101

[25] Miller D C, Herrmann C F, Maier H J, George S M, Stoldt C R and Gall K 2005 *Scr. Mater.* **52** 873

[26] Liu B and Terano M 2001 *J. Mol. Catal A-Chem.* **172** 227

[27] Surviliene S, Jasulaitiene V, Cesuniece A and Lisowska-Oleksiak 2008 *Solid State Ionics* **179** 222

[28] Vancea J, Reiss G, Schneider F, Bauer K and Hoffmann H 1989 *Surf. Sci.* **218** 108

[29] Gaspar A B, Perez C and Dieguez L 2005 *Appl. Surf. Sci.* **252** 939

[30] Desimoni E, Malitesta C, Zambonin P and Riviere J 1988 *Surf. Interface Anal.* **13** 173

[31] Kim J and Hummel R 1990 *Phys. Status Solidi A* **122** 255

[32] Gardner D S and Flinn P A 1990 *J. Appl. Phys.* **67** 1831

[33] Harris K E and King A H 1994 *A tem investigation of the effects of tensile stress on thin film microstructure and surface morphology* (London: Cambridge University Press) p. 75

[34] Mullins W 1958 *Acta Metall. Sin.* **6** 414