Residual stress induced wetting variation on electric brush-plated Cu film*

Meng Ke-Ke(孟可可), Jiang Yue(江 月), Jiang Zhong-Hao(江忠浩)†, Lian Jian-She(连建设), and Jiang Qing(蒋 青)

Key Laboratory of Automobile Materials, Department of Materials Science and Engineering, Jilin University, Changchun 130025, *China*

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Nanocrystalline Cu film with a mirror surface finishing is prepared by the electric brush-plating technique. The as-prepared Cu film exhibits a superhydrophilic behavior with an apparent water contact angle smaller than 10°. A subsequent increase in the water contact angle and a final wetting transition from inherent hydrophilicity with water contact angle smaller than 90° to apparent hydrophobicity with water contact angle larger than 90° are observed when the Cu film is subjected to natural aging. Analysis based on the measurement of hardness with nanoindentation and the theory of the bond-order-length-strength correlation reveals that this wetting variation on the Cu film is attributed to the relaxation of residual stress generated during brush-plating deposition and a surface hydrophobization role associated with the broken bond polarization induced by surface nanostructure.

Keywords: superhydrophilicity, wetting transition, residual stress, nano indenter

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1. Introduction

Wettability with a liquid is one of most important properties of solid surfaces, which is governed mainly by surface roughness and surface energy.[1] Recently, special wettability including superhydrophilicity and superhydrophobicity, and switchable wettability between hydrophilicity and hydrophobicity, have attracted much interest due to their great significances in both fundamental research and practical applications in various fields such as self-cleaning, drug delivery, and intelligent switch.[2,3] Generally, the special and switchable wettability are obtained on solid surfaces by combining micro/nanostructures with certain functional polymers, in conjunction with external stimulation, such as UV irradiation and electric field.[4–9] Various deposition techniques, such as electroless deposition,[10,11] electrochemical deposition,[12,13] and physical/chemical vapor deposition,[14,15] are potentially useful for the fabrication of required surface structures and modification layers for the special and switchable wettability. However, these deposition techniques often induce residual stress including tensile and compressive stresses in the deposited films,[16–22] which can affect not only their mechanical properties (e.g., hardness and strength), but also some physical properties (e.g., photoluminescence and photocatalysis) due to the distortion of the crystalline structure.[23–28] Furthermore, the presence of residual stress can lead to structural change of deposited films (e.g., stress corrosion or film cracking).[29,30] Therefore, it is expected that the residual stress associated with excess energy will affect the surface wettability of deposited films. Nevertheless, the relationship between surface wettability and residual stress has not been established yet.

Metals widely used in many industrial and daily-life fields are typically hydrophilic materials. Nearly all liquids tend to spread on metallic surfaces due to their high native surface energy. Recently, massive efforts have been devoted to fabricate metallic surfaces with the special and switchable wettability by using various deposition techniques.[10–13] Meanwhile, the metallic films will suffer residual stress during deposition, which can be relaxed by recrystallization and grain growth under certain conditions, such as thermal cycling, heat treatment, and natural aging.[31–34] It has been suggested that the relaxation of residual stress is accompanied by the decrease in Gibbs free energy of system.[35,36] Therefore, it is of both theoretical and practical significance to fabricate a metallic surface with special and/or switchable wettability in a certain stress (energy) state. In this paper, we fabricated a nanocrystalline Cu film with a mirror surface finishing by the electric brush-plating technique.[37] A special wettability (i.e., superhydrophilicity) and a wettability transition from hydrophilicity to hydrophobicity were obtained on the Cu film due to the relaxation of residual stress generated during the brush-plating deposition and a surface hydrophobization role associated with the broken bond polarization induced by the surface nanostructure.

2. Experimental details

Nanocrystalline Cu film was fabricated on smooth Cu sheets by an electric brush-plating technique using bath mainly containing copper sulfate pentahydrate (260 g/l), ammonium nitrate (30 g/l), citric acid monohydrate (3 g/l), and a few additives. The electric brush-plating operation was performed un-

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†Corresponding author. E-mail: jzh@jlu.edu.cn

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der a brush-plating voltage of 6 V at room temperature (298 K) with a deposition rate of $\sim$ 0.06 mm/h. The brush-plating voltage was supplied by a direct current power pack (DSD-75-S). After brush-plating, the Cu film was washed with absolute ethyl alcohol and deionized water followed by drying in a stream of N_2. Finally, the natural aging treatment of the as-prepared Cu film was conducted in a drying oven at the ambient condition for different times.

The surface morphology of the Cu film was observed by the field emission scanning electron microscope (FESEM) (JSM-6700F, JEOL, Japan). The surface chemical composition of the Cu film was analyzed by the energy dispersive X-ray spectrometer (EDS) (X-Max, Oxford, Germany). The microstructure of the Cu film was characterized by the transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan). The wettability of the Cu film was evaluated by the water contact angle (WCA) measurement using the circle fitting on an optical contact angle meter (OCA20, Dataphysics, Germany) at room temperature (298 K). The surface hardness of the Cu film was measured by performing the nanoindentation test on a nanoindenter instrument (G200, Agilent, USA) with a Berkovich diamond indenter. The Cu film was indented at a loading strain rate of 10^{-2} s^{-1}, an indenter depth of 800 nm, and a holding time of 10 s. Indentation was repeated at least eight times for each measurement. The residual stress of the Cu film was evaluated by using the data of the hardness and the approach proposed by Suresh and Giannakopoulos.[38] It has been shown that the residual stress generated in the electrodeposited Cu films is almost independent of the film thickness when it exceeds a certain value ($\sim$ 10 μm).[19] Considering this factor, the requirement of the indentation measurement for the ratio of indenter depth to film thickness (<10%),[39] and the requirement for available application, the thickness of the Cu film was chosen as $\sim$ 20 μm.

3. Results and discussion

The FESEM images in Figs. 1(a) and 1(b) show that the Cu film exhibits a quite uniform grain structure with size of 30-50 nm, indicating that the Cu film has a mirror surface finishing. The cross-section FESEM image of the Cu film in the inset of Fig. 1(a) shows that the thickness of the Cu film is $\sim$ 20 μm (indicated by the white arrow). The EDS spectrum in the inset of Fig. 1(b) shows that the surface of the Cu film was oxidized slightly in air. The TEM observation of the grain structure in Fig. 1(c) shows roughly equiaxed grains separated by predominant high-angle grain boundaries. The pattern of the selected area electron diffraction in the inset of Fig. 1(c) reveals random crystallographic orientation and a fine grain structure. The statistical grain size distribution taken from the TEM images shows an average grain size of $\sim$ 35 nm, which is consistent with the FESEM observation (Fig. 1(b)). Most of the grains contain a high density of twins (Figs. 1(c) and 1(d)).

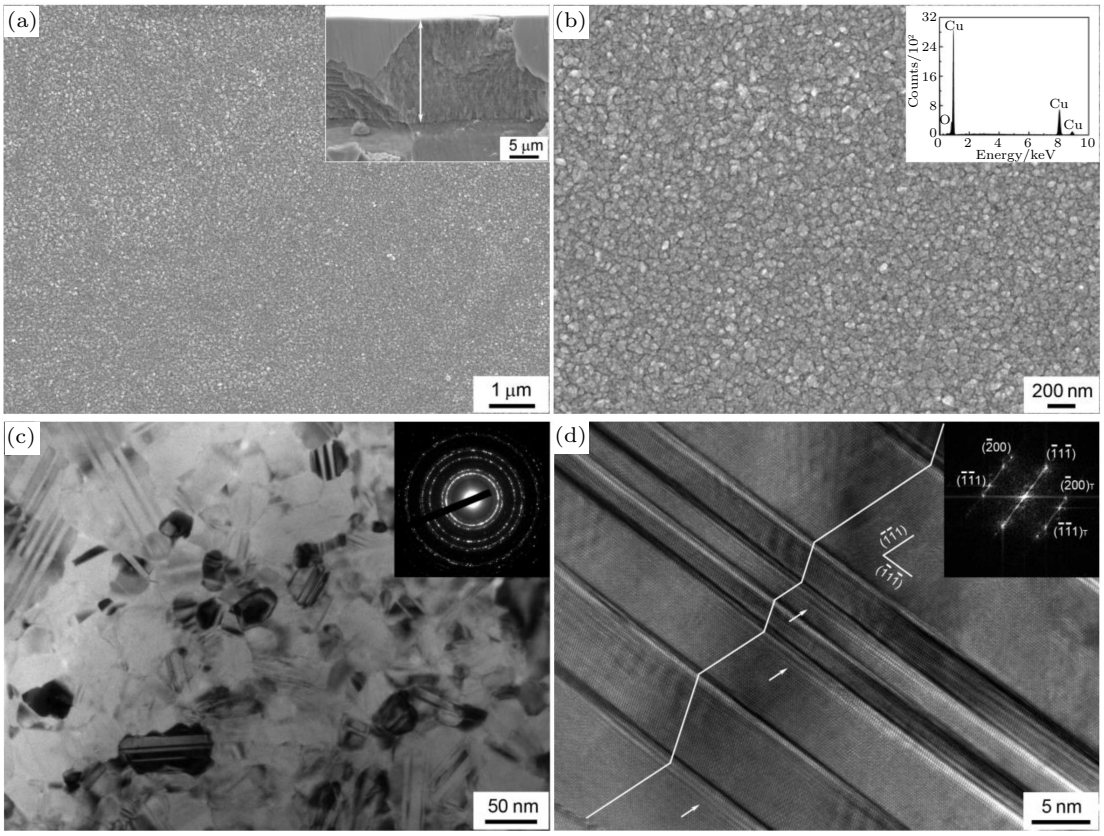


Fig. 1. (a) Surface and cross-section (inset) FESEM images of the Cu film. (b) Surface FESEM image and EDS spectrum (inset) of the Cu film. (c) Bright field TEM image and selected area electron diffraction pattern (inset) of the Cu film. (d) High-resolution TEM image and selected area electron diffraction pattern (inset) of the Cu film.

The accompanying diffraction pattern shows diffraction spots caused by twinning (inset of Fig. 1(d)). The statistical measurement of the twin lamella thickness shows a narrow distribution ranging from several to several tens nanometers, with an average value of ~ 15 nm. The high-resolution TEM observation indicates that some dislocations and stacking faults are located at the twin boundaries (indicated by the white arrows in Fig. 1(d)).

The wettability of the Cu film is evaluated by the WCA measurement and the results are shown in Fig. 2. It can be seen that the Cu film in the as-prepared state exhibits a superhydrophilic behavior with a WCA of $\sim 9°$, which is significantly smaller than that on the smooth native Cu surface ($\sim 63°$[12]), although the surface of the Cu film is also considerably smooth (i.e., a mirror surface finishing). As the natural aging time increases, the WCA of the Cu film increases and exceeds the equilibrium value (63°) when the natural aging time exceeds ~ 3.7 days and exceeds the critical WCA value between hydrophilicity and hydrophobicity (90°) when the natural aging time exceeds ~ 5.6 days. Finally, the WCA of the Cu film reaches a maximum value of 102° when the natural aging time increases to 8 days. We also observe that the wettability of the Cu film no longer changes significantly when the natural aging time is larger than 8 days (which is not presented in Fig. 2).

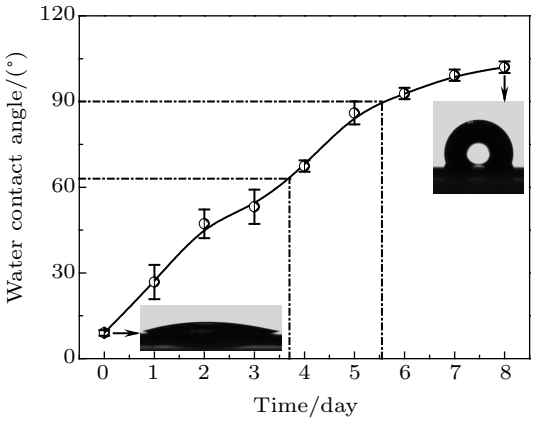


Fig. 2. Variation of water contact angle of the Cu film with natural aging time.

Nanoindentation is a very powerful method for characterizing mechanical properties (hardness, elastic modules, residual stress, etc) of thin films.[23,24,38,40] Figure 3(a) shows the representative load-displacement (P–h) curves of the Cu film at different natural aging times. As shown in the loading regime, the load required for a given indenter depth increases with increasing natural aging time. This suggests the presence of a residual tensile stress generated during the brush-plating deposition and its significant contribution to the load level or hardness of the Cu film.[23,24,38] Based on the approach proposed by Suresh and Giannakopoulos,[38] the residual tensile stress generated in the Cu film can be evaluated by the P–h data using the following equation:

$$A/A' = (1 + \sigma_{\mathrm{R}}/P_{\mathrm{ave}})^{-1}, \tag{1}$$

where $A = P_{\max}/P_{\mathrm{ave}}$ and $A' = P'_{\max}/P_{\mathrm{ave}}$ are the projected contact areas on the indented material surface in the stress state and in the stress-free state, respectively; σ_{R} is the residual stress; P_{ave} is the average contact pressure and is equal to the hardness of the indented material H, which remains invariant because elastic residual stress does not change the magnitude of plastic strain.[38] The $P_{\max}$ and $P'_{\max}$ are the maximum loads on the indented material surface in the stress state and in the stress-free state, respectively. The σ_{R} as a function of $P_{\max}$ can be thus given by

$$\sigma_{\mathrm{R}} = (P'_{\max}/P_{\max} - 1)H. \tag{2}$$

For the Cu film, H is determined to be 2.12 GPa according to the load data given by the nanoindentation. The Cu film with the natural aging time of 8 days is approximately regarded as staying in the stress-free state. The corresponding $P'_{\max}$ is thus determined to be ~ 31.87 mN. Using these two data, the variation of σ_{R} with $P_{\max}$ or with the natural aging time are finally determined based on Eq. (2) and is shown in Fig. 3(b).

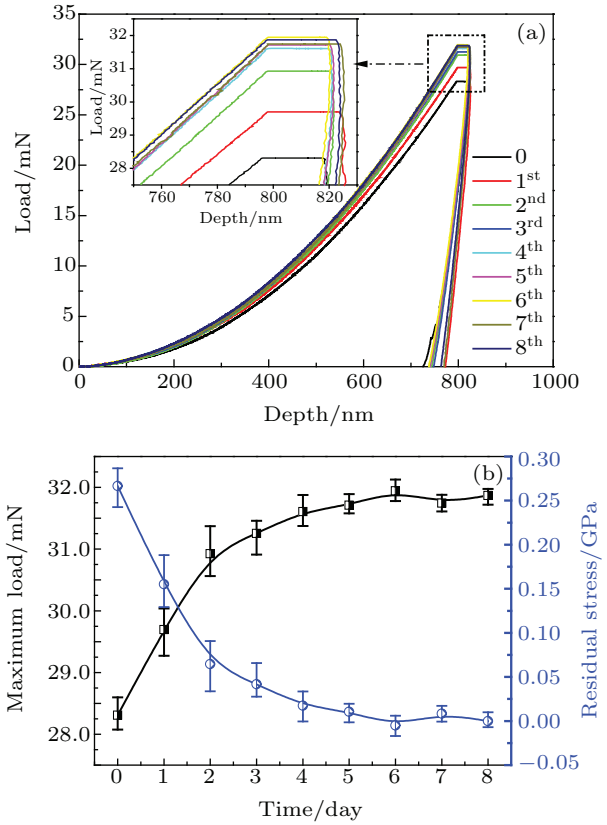


Fig. 3. (color online) (a) Load-displacement (P–h) curves obtained at a loading strain rate of 10^{-2} s^{-1}, an indenter depth of 800 nm, and a holding time of 10 s; (b) variations of the maximum load and calculated residual stress for the Cu film with natural aging time.

It can be observed that with the increase in the natural aging time, the maximum load on the Cu film increases, while the corresponding residual stress changes along the reverse direction. The Cu film in the as-prepared state has a maximum residual stress of about ~ 0.267 GPa for the natural aging time of 0 day. As the natural aging time increases, the residual

stress in the Cu film first decreases sharply by $\sim 76\%$ for the natural aging time of 0–2 days and then decreases relatively slowly for the natural aging time of 2–5 days. When the natural aging time is ~ 5 days, the residual stress in the Cu film reaches a value close to zero. When the natural aging time is larger than ~ 5 days, the residual stress in the Cu film no longer changes significantly.

Because the Cu film is deposited on the Cu sheet and low heat is produced during the brush-plating deposition, the macro-level residual stress along the film thickness direction would be very small and thus can be neglected. Therefore, the residual stress generated during the brush-plating deposition arises mainly from the volume contraction of the Cu crystals caused by the coalescence of Cu atoms and the formation of grain boundaries.[19,36] The neighboring Cu atoms pull each other, giving rise to a biaxial tensile stress. Furthermore, the fine grains of the Cu film generate a large volume of grain boundaries, which can enhance further the tensile stress due to the relatively random arrangement of Cu atoms.[22] After the Cu film grows to the required thickness, the generated tensile stress will remain in the as-prepared Cu film in the form of residual stress.

The presence of residual stress in deposited films is accompanied by the distortion of the crystalline structure.[27] During the natural aging, the residual stress in the as-prepared Cu film will be relaxed and the distortion of the crystalline structure will be partly eliminated. From a thermodynamic point of view, this relaxation of the residual stress will lead to the decrease in the Gibbs free energy of the system and hence the surface energy of the Cu film. This effect of the residual stress on the Gibbs free energy of the system has been revealed in recent simulation and experimental studies.[35,36] Simulation study[35] suggested that the Gibbs free energy of Cu will significantly increase when it is subjected to a biaxial tensile stress. Experimental study[36] revealed that a high residual tensile stress can be generated during the electrodeposition of a Cu film, and the relaxation of the residual stress can reduce the Gibbs free energy of the system and eliminate partly the distortion of crystalline structure, thus leading to the formation of a nanotwin structure.

The wettability of solid surfaces is governed mainly by two factors, i.e., surface roughness and surface energy.[1] Because the surface roughness of the Cu film does not change during the natural aging, the increase in the WCA with the natural aging time should be attributed to the decrease in the surface energy caused by the relaxation of the residual stress generated during the brush-plating deposition. This can explain the increase in the WCA with the natural aging time lasting till ~ 3.7 days, where the residual stress is almost fully relaxed and the corresponding WCA reaches an equilibrium value comparable to that on the smooth native Cu surface ($\sim 63^\circ$[12]). The subsequent increase in the WCA of the Cu film should be irrelevant to the relaxation of the residual stress. A possibility leading to this increase in the WCA after full relaxation of the residual stress is a surface hydrophobization role caused by the surface nanostructure. From the perspective of physical forces or chemical bonds, the wettability reflects the interplay between molecules and/or atoms of solids and liquids. When the size of the surface structure reduces to nanometer scale, the atomic and molecular details of solids and liquids become significant. According to the bond-order-length-strength (BOLS) correlation theory proposed by Sun,[41,42] the densely- and tightly-trapped bonding charges polarize the existing surface nonbonding electrons to form locally locked skin monopoles. In addition, the surface oxidation during natural aging makes new stringer O–Cu bonds form on the surface of the Cu film. The sp-orbit hybridization of oxygen upon reacting with Cu atoms generates nonbonding lone pairs or unpaired edge electrons that induce locally locked skin dipoles on the surface of the Cu film.[41,42] The Coulomb repulsion between the monopoles or dipoles locked in the counterparts of the nano-sized solid–liquid contact may suspend the droplet with air trapped below it, just like a "magnetic levitation train" or a "hovercraft", which would weaken the interfacial attraction between the Cu film and water and thus render the Cu film hydrophobic. Therefore, the surface broken bond polarization induced by the surface nanostructure can provide a reasonable explanation for the subsequent increase in the WCA and the final wetting transition from inherent hydrophilicity (WCA smaller than 90°) to apparent hydrophobicity (WCA larger than 90°) observed on the stress-free Cu film. It would be expected that the above surface hydrophobization role has a relatively weak dependence on the natural aging time as compared to that of the residual stress, because the amount of the stringer O–Cu bonds is limited on the nanostructured surface of the Cu film. Thus, this surface hydrophobization role dominates the increase in the WCA of the Cu film when the residual stress is fully relaxed, while the relaxation of the residual stress plays a main role in increasing the WCA in the initial natural aging stage.

4. Conclusion

We have fabricated a nanocrystalline Cu film with a mirror surface finishing by the electric brush-plating technique. The as-prepared Cu film exhibited a superhydrophilic behavior with an apparent WCA smaller than 10°. A subsequent increase in the WCA and a final wetting transition from inherent hydrophilicity to apparent hydrophobicity are observed when the Cu film is subjected to the natural aging. Our analysis based on the hardness measurement and the BOLS correlation theory reveals that this wetting variation on the Cu film is attributed to the relaxation of the residual stress generated by the coalescence of Cu atoms and the formation of an amount of grain boundaries during the brush-plating deposition and a surface hydrophobization role associated with the broken bond polarization induced by the surface nanostructure.

References

[1] Jiang L, Wang R, Yang B, Li T J, Tryk D A, Fujishima A, Hashimoto K and Zhu D B 2000 *Pure Appl. Chem.* **72** 73
[2] Feng X J and Jiang L 2006 *Adv. Mater.* **18** 3063
[3] Bhushan B and Jung Y C 2011 *Prog. Mater. Sci.* **56** 1
[4] Feng X J, Zhai J and Jiang L 2005 *Angew. Chem. Int. Ed.* **44** 5115
[5] Gu C D, Zhang J and Tu J P 2010 *J. Colloid Interf. Sci.* **352** 573
[6] Gong M G, Xu X L, Yang Z, Liu Y S and Liu L 2010 *Chin. Phys. B* **19** 056701
[7] Powell M R, Cleary L, Davenport M, Shea K J and Siwy Z S 2011 *Nat. Nanotech.* **6** 798
[8] Yang Z, Wu Y Z, Ye Y F, Gong M G and Xu X L 2012 *Chin. Phys. B* **21** 126801
[9] Wang G Y and Zhang T Y 2012 *J. Colloid Interf. Sci.* **377** 438
[10] Larmour I A, Bell S E J and Saunders G C 2007 *Angew. Chem. Int. Ed.* **46** 1710
[11] Gu C D, Ren H, Tu J P and Zhang T Y 2009 *Langmuir* **25** 12299
[12] Wang S T, Feng L, Liu H, Sun T L, Zhang X, Jiang L and Zhu D B 2005 *Chem. Phys. Chem.* **6** 1475
[13] Wang G Y and Zhang T Y 2012 *ACS Appl. Mater. Interfaces* **4** 273
[14] Gong M G, Xu X L, Cao Z L, Liu Y Y and Zhu H M 2009 *Acta Phys. Sin.* **58** 1885 (in Chinese)
[15] Liu H, Feng L, Zhai J, Jiang L and Zhu D B 2004 *Langmuir* **20** 5659
[16] Hurtos E and Rodriguez-Viejo J 2000 *J. Appl. Phys.* **87** 1748
[17] Song J Y and Yu J 2002 *Thin Solid Films* **415** 167
[18] Kong D J, Zhang Y K, Chen Z G, Lu J Z, Feng A X, Ren X D and Ge T 2007 *Acta Phys. Sin.* **56** 4056 (in Chinese)
[19] Kima S, Jang J H, Lee J S and Duquette D J 2007 *Electrochim. Acta* **52** 5258
[20] Saitou M, Oshiro S and Sagawa Y 2008 *J. Appl. Phys.* **104** 093518
[21] Cen M, Zhang Y G, Chen W L and Gu P F 2009 *Acta Phys. Sin.* **58** 7025 (in Chinese)
[22] Shao I, Romankiw L T and Bonhote C 2010 *J. Cryst. Growth* **312** 1262
[23] Schall J D and Brenner D W 2004 *J. Mater. Res.* **19** 3172
[24] Wang L, Bei H, Gao Y F, Lu Z P and Nieh T G 2011 *Acta Mater.* **59** 2858
[25] Shibata T, Irie H and Hashimoto K 2003 *J. Phys. Chem. B* **107** 10696
[26] Qu Y H, Jiang D S, Wu D H, Niu Z C and Sun Z 2005 *Chin. Phys. Lett.* **22** 2088
[27] Shibata T, Irie H, Tryk D A and Hashimoto K 2009 *J. Phys. Chem. C* **113** 12811
[28] Wei W, Liu M, Qu S W and Zhang Q Y 2009 *Acta Phys. Sin.* **58** 5736 (in Chinese)
[29] Michalske T A and Freiman S W 1982 *Nature* **295** 511
[30] Sun H L, Song Z X and Xu K W 2008 *Acta Phys. Sin.* **57** 5226 (in Chinese)
[31] Thouless M D, Gupta J and Harper J M E 1993 *J. Mater. Res.* **8** 1845
[32] Lingk C and Gross M E 1998 *J. Appl. Phys.* **84** 5547
[33] Moriyama M, Matsunaga K, Morita T, Tsukimoto S and Murakami M 2004 *Mater. Trans.* **45** 3033
[34] Hwang S J, Lee Y D, Park Y B, Lee J H, Jeong C O and Joo Y C 2006 *Scripta Mater.* **54** 1841
[35] Xu D, Kwan W L, Chen K, Zhang X, Ozoliņš V and Tu K N 2007 *Appl. Phys. Lett.* **91** 254105
[36] Xu D, Sriram V, Ozolins V, Yang J. M, Tu K. N, Stafford G R and Beauchamp C 2009 *J. Appl. Phys.* **105** 023521
[37] Jiang Z H, Zhang H Z, Gu C D, Jiang Q and Lian J S 2008 *J. Appl. Phys.* **104** 053505
[38] Suresh S and Giannakopoulos A E 1998 *Acta Mater.* **46** 5755
[39] Kramer D E, Volinsky A A, Moody N R and Gerberich W W 2001 *J. Mater. Res.* **16** 3150
[40] Mu J W, Jiang Z H, Zheng W T, Tian H W, Lian J S and Jiang Q 2012 *J. Appl. Phys.* **111** 063506
[41] Sun C Q, Sun Y, Ni Y G, Zhang X, Pan J S, Wang X H, Zhou J, Li L T, Zheng W T, Yu S S, Pan L K and Sun Z 2009 *J. Phys. Chem. C* **113** 20009
[42] Sun C Q 2009 *Prog. Mater. Sci.* **54** 179