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Morphology of brass films sputtered on celloidin substrate towards high-gloss pigment

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Abstract

Film-transition technique is put forward to manufacture high-gloss metallic pigment. The effect of chamber pressure, target-to-substrate distance and sputtering voltage on morphology of brass film sputtered on celloidin substrate has been studied with atomic force microscopy and surface glossmeter. Polycrystalline films with different roughness are obtained through changing the sputtering conditions. The results show that all of the brass films have ellipsoidal surface, well-ordered grain orientation, large grain size and uniform grain distribution, resulting in low surface roughness and high surface luster of brass films. At the condition of chamber pressure 15 Pa, target-to-substrate distance 3.4 cm, sputtering voltage 1.5 kV and sputtering time 30 min, the brass film with thickness 41 nm, Cu content 69.5–73.6%, surface roughness 4.85 nm and surface gloss 136.7 Gs is deposited, revealing the great possibility for high-gloss metallic pigment.

Keywords: Morphology; Sputtering; Thin film; Surface gloss; Brass; Metallic pigment

1. Introduction

Metallic films have been widely used in chemistry, catalysis and semiconductor industries [1–5]. Recently, we have paid great attention to the growth of metallic films on soluble substrates because metallic films can be used to manufacture micromirror-like metallic pigments through vigorous stirring or ultrasonic treatment [6–10]. Both thickness and smoothness are very important for optical properties of metallic pigment. In traditional ball-milling process, micromirror-like pigment is very hard to manufacture because of its irregular thickness and much surface defects existed on metallic flakes. Usually, favorable thickness is about 30–50 nm. If the thickness is above 50 nm, the orientation ability of the pigments is negatively influenced and the scattering effects at the edges of the pigments increase. Both effects have a negative impact on brilliance, opacity and flop of metallic coating. If the thickness is below 30 nm, powders may become transparent and moreover its handling may be difficult due to high agglomeration tendencies. Surface smoothness positively influences the reflectance of metallic coating. Films, if prepared through physical vapor deposition (PVD), have the advantage of uniform thickness and ideal smoothness over traditional mechanical process [1–13]. To obtain metallic nanofilm, soluble substrate is necessary. The possible soluble substrate is resin systems, such as cellulose, acrylics and vinyl resins. Thus, after brass/soluble substrate structures have been treated with solvent in stripper, in which the releasable substrate is dissolved and then the brass film is separated from suspended liquor as fragments or coarse flakes. The solvent used in the stripper depends on the solubility of substrate. The brass fragments or coarse particles are washed and concentrated, if desired, to a dispersion normally containing 10–20% pigment. Finally the particles are sized by vigorous stirring or ultrasonic treatment. PVD pigments possess identical thickness and rare surface defects, therefore guaranteeing a high level of specular reflectance. In our previous research [6–8], we have investigated the growth and surface morphology of brass film on acrylics and glass substrate. However, glass substrate

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has no feasibility because of its infusibility, and acrylics have the disadvantage of low melting point. Celloidin is a good substrate because its melting point is much higher than that of acrylics, furthermore it can rapidly form thin film and the thin film can dissolve into ester solvent such as ethyl acetate. So far, there is no report on growth of brass film on celloidin substrate towards high-gloss brass pigment.

2. Experimental method

The experiment was performed in a custom-designed sputtering chamber. A mechanically polished brass target was cleaned by repeated Ar^+ sputtering and then annealed at 520 °C in order to remove impurities. Celloidin film attached on filter cloth was used as soluble substrate. Chamber pressure was measured with thermocouple vacuum gauge. The substrate temperature was monitored with a chromel–alumel thermocouple, which was spot-welded on a Ta sheet attached to the substrate. In the sputtering process, substrate temperature was controlled around 130 °C.

The analysis of brass target was performed with X-ray fluorescence spectroscopy (XRFS). The results are shown in Fig. 1. The intensities of Cu and Zn are 676 kCPS and 280.3 kCPS, respectively. The main impurity is Fe and its intensity is 0.8 kCPS. The contents of Cu and Zn in brass target are 70.6% (mass fraction) and 29.3%, respectively, and total content of impurities is not more than 0.1%. To obtain average thickness and Cu content of brass films, chemical/physical analysis is applied. Firstly, brass film is separated from brass/celloidin system through the dissolution of celloidin substrate with ethyl acetate, and then dissolved with 6.5% nitric acid. The solution concentration was measured with ICP-AES. Finally, the thickness and Cu content are calculated through material balance. WinSPM type AFM is applied to investigate the surface morphology. XGT type glossmeter was used to measure the surface gloss, in which incidence angle is settled at 60°.

3. Results and discussion

The analysis of constitution of brass film sputtered on celloidin substrate at 130 °C shows that the content of Cu varies in the range of around 69.5–73.6% regardless of the great difference in chamber pressure, target-to-substrate distance and sputtering voltage.

The effect of chamber pressure on morphology of brass films deposited on celloidin substrate at 130 °C for 30 min is shown in Fig. 2(a,b). When the chamber pressure increased from 15 Pa to 20 Pa, the surface roughness increased from 4.85 nm to 15.5 nm. At high pressure, because of short mean free path and large collision odds with Ar^+, sputtering atoms have low average kinetic energy and large horizontal velocity. On the one hand, low kinetic energy decreases the transport ability of sputtering atoms on soluble substrate. On the other hand, large horizontal velocity decreases filling probability. Furthermore, too much sputtering atoms result in difficulty in the diffusion and distribution. So, at high pressure, rough surface and much grain boundaries might be formed.

When the target-to-substrate distance shortens from 3.4 cm to 2 cm, the surface roughness increase from 4.85 nm to 6.7 nm (Fig. 2(a,c,d)). When target-to-substrate distance is small, brass film surface may be rough or uneven because some nanofilm surface probably broke under the collision of sputtering atoms with high kinetic energy.

When the sputtering voltage decreases from 1.5 kV to 1.2 kV, the surface roughness decrease from 4.85 nm to 4.44 nm (Fig. 2(a,e)). On the one hand, high voltage means large accelerating electric field, high kinetic energy, large transport ability and large deposition rate. Large deposition rate makes the adsorbed alloy atoms hard to diffuse and distribute on celloidin surface on time. On the other hand, high kinetic energy might provide much probability of damage to film surface.

The pivotal factor affecting the morphology of brass nanofilm is the kinetic energy of sputtering atoms. High kinetic energy means high deposition rate, which probably makes adsorbed atoms hard to diffuse and distribute uniformly on time or even cause damage to brass film surface, and then produces uneven nanofilm surfaces. Low voltage, large target-to-substrate distance and low pressure are necessary for smooth surface. Taking account of growth rate and surface roughness, the optimal sputtering condition is as follows: sputtering voltage 1.5 kV, target-to-substrate distance 3.4 cm and chamber

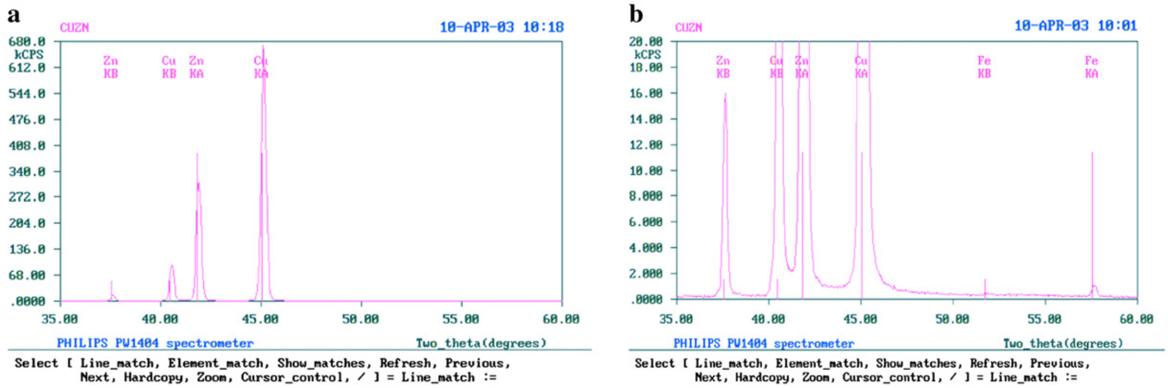

Fig. 1. XRF analysis of brass target. (a) XRF and (b) enlarged XRF.

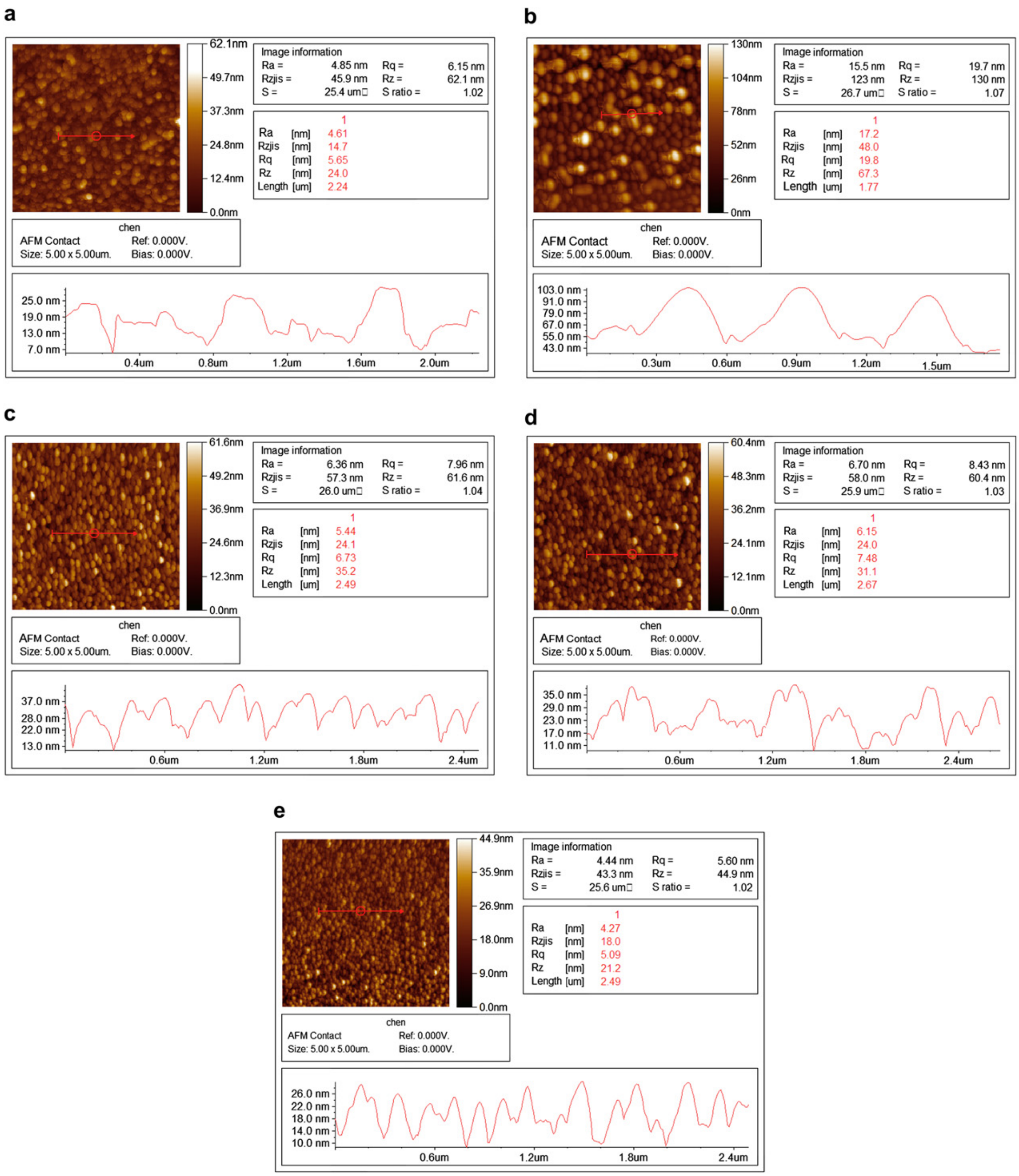

Fig. 2. AFM images of brass film under different conditions. (a) 15 Pa, 3.4 cm, 1.5 kV; (b) 20 Pa, 3.4 cm, 1.5 kV; (c) 15 Pa, 2.5 cm, 1.5 kV; (d) 15 Pa, 2 cm, 1.5 kV; (e) 15 Pa, 3.4 cm, 1.2 kV.

pressure 15 Pa. If sputtered for 30 min at substrate temperature 130 °C on celloidin substrate, brass film with thickness 41 nm and surface roughness 4.85 nm will be deposited.

Fig. 3 is the enlarged AFM images of brass film grown on celloidin substrate. It shows that the grain distribution and grain size are rather uniform (Fig. 3(a,b,c)). Especially, the grains look like ellipsoidal mirror; grain size is as large as 100 nm $\times$ 200 nm (Fig. 3(d,e)) and grain orientation is parallel to each other. The near-planar ellipsoidal surface, well-ordered grain structure and large grain size are very favorable for metallic pigment because each grain means a micromirror to some extent; and then light scattering can be decreased to the lowest extent. If polishing is accompanied after brass film is crushed up into slice-like brass powder, high-gloss brass powder can be prepared. It is very interesting that the grain orientation and grain distribution in these brass films are very similar to each other regardless of the great difference in chamber pressure, target-to-substrate distance and sputtering voltage.

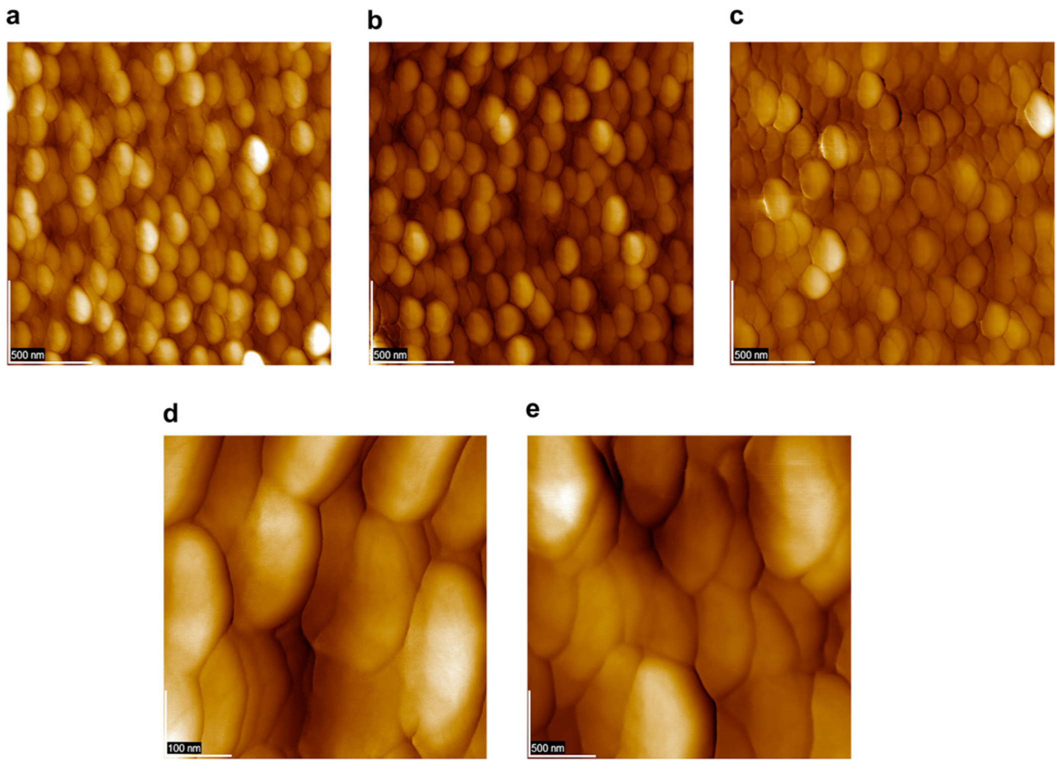

Fig. 3. Enlarged AFM images of brass film under different conditions. (a) 15 Pa, 3.4 cm, 1.5 kV; (b) 15 Pa, 2.5 cm, 1.5 kV; (c) 15 Pa, 2.0 cm, 1.5 kV; (d) 15 Pa, 3.4 cm, 1.5 kV; (e) 15 Pa, 2.0 cm, 1.5 kV.

Surface gloss is the most important factor for metallic pigment. Surface gloss is the integrated function of grain size, grain morphology, grain orientation and grain distribution. To obtain more information about the surface morphology of brass film deposited on celloidin substrate, the surface gloss of brass films deposited at different sputtering conditions is measured. The results of surface gloss show that surface gloss is closely in accordance with surface roughness, which means

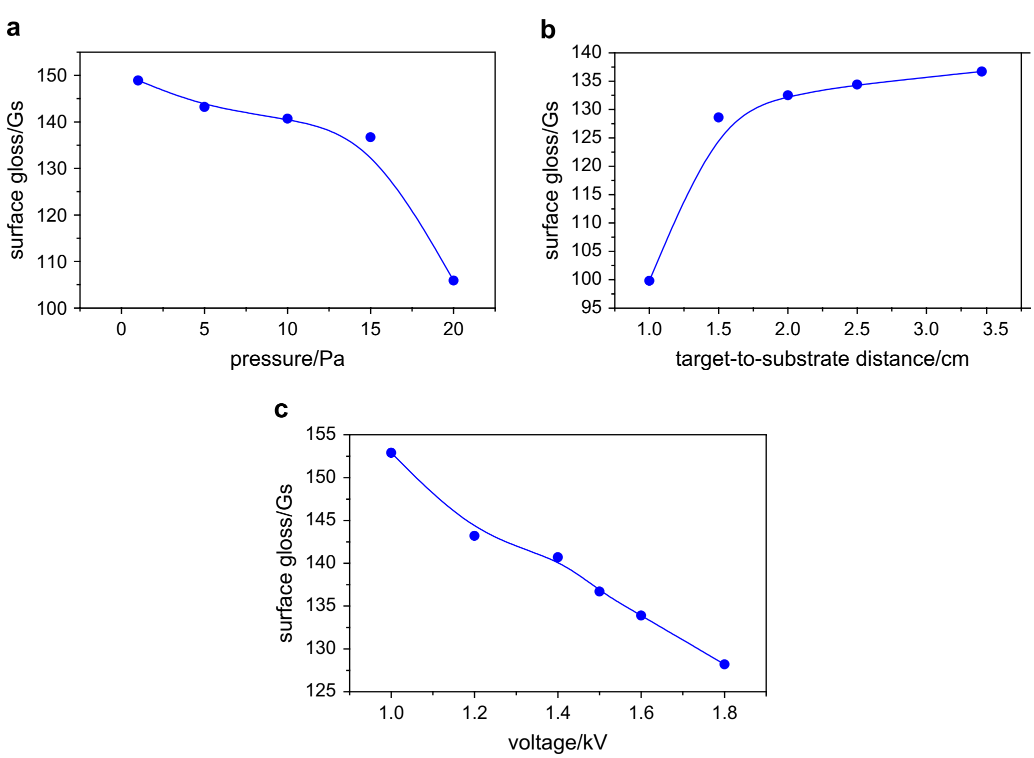

Fig. 4. The effect of pressure, target-to-substrate distance and voltage on surface gloss of brass film. (a) 3.4 cm, 1.5 kV; (b) 15 Pa, 1.5 kV; (c) 15 Pa, 3.4 cm.

that the higher the roughness is, the higher the surface gloss will be. With the increase of pressure, surface gloss gradually decreases (Fig. 4(a)). With the augment of target-to-substrate distance, surface gloss gradually increases (Fig. 4(b)). With the increase of voltage, surface gloss gradually decreases (Fig. 4(c)).

4. Conclusions

The brass films sputtered on celloidin substrate at 130 °C possess the characteristics of well-ordered grain orientation, uniform grain distribution, large grain size and ellipsoidal morphology regardless of the great difference in chamber pressure, target-to-substrate distance and sputtering voltage. Low chamber pressure, large target-to-substrate distance and low sputtering voltage are hopeful for good surface smoothness because of less damnification or defect. Surface gloss of brass films mainly depends on surface roughness. Under the condition of sputtering voltage 1.5 kV, target-to-substrate distance 3.4 cm, chamber pressure 15 Pa and sputtering time 30 min, high-gloss brass films with thickness 41 nm, Cu content 69.5–73.6%, surface roughness 4.85 nm and surface gloss 136.7 Gs, is obtained.

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