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LETTER

A Composite Additive used for an Excellent New Cyanide-free Silver Plating Bath

Cite this: DOI: 10.1039/c3nj00000x

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Received 00th XXXXX 2013,
Accepted 00th XXXXX 2013

DOI: 10.1039/c3nj00000x

www.rsc.org/njc

An effective composite additive used for an investigated cyanide-free silver plating bath was introduced. Mirror bright silver deposits with excellent leveling capability as well as smooth and compact morphology could be obtained from the investigated cyanide-free bath in the presence of the introduced composite additive.

Silver deposit is one of the most important forms of silver applied in microelectronics, aerospace, automotive, and jewelries¹⁻⁵. For more than 100 years, cyanide based electroplating baths for silver electrodeposition are widely used due to their low cost with excellent physiochemical properties, good corrosion resistance, high bulk conductivity, and excellent welding performance⁶⁻⁹. Unfortunately, cyanide is one of the most toxic chemicals, which brings extremely high risks to human health and the environment.¹⁰ A number of cyanide-free silver plating baths based on thiosulfate¹¹⁻¹⁴, uracil¹⁵, and 2-hydroxypyridine^{16, 17} as complexing agents have been investigated to overcome these challenges in recent years. However, except for few successful cases, most of these baths still suffer from problems of not being able to produce deposit with good quality. Using additive is an effective way to solve these problems and obtain silver deposit with satisfactory performance and reliability¹⁸.

5,5-dimethylhydantoin (DMH) and nicotinic acid (NA) were selected as complexing agents for silver electroplating in our study¹⁹. Silver deposits on copper substrates with excellent leveling capability, smooth and compact morphologies, high purity and conductivity, as well as excellent welding property could be electroplated from this unique bath. Based on the performances of the plating bath and silver deposit, the DMH and NA based silver plating bath is a promising candidate for silver electrodeposition to replace the conventional cyanide based silver electroplating baths. In order to improve the practicability with higher production efficiency, the cyanide-free silver plating bath was modified on the concentration of AgNO₃ and the plating conditions.

In present paper, a composite additive containing 2,2'-Bipyridine and Potassium antimonyl tartrate used for the DMH and NA based silver plating bath was studied and introduced briefly. The effect of the composite additive on the performances of silver deposit and the

plating bath was investigated from the point of the morphologic and electrochemical views.

2,2'-Bipyridine and Potassium antimonyl tartrate were used as the composite additive for the DMH and NA based cyanide-free silver plating bath. Effect of the additive on the appearance of the silver electrodeposit was studied. Fig. 1 displays the macroscopic images of silver deposits obtained from the cyanide-free bath with and without additive. The silver deposits in Fig 1 (a) and (c) were obtained from basic bath, respectively. While the bath with additive was used to prepare silver deposits in Fig 1 (b) and (d).

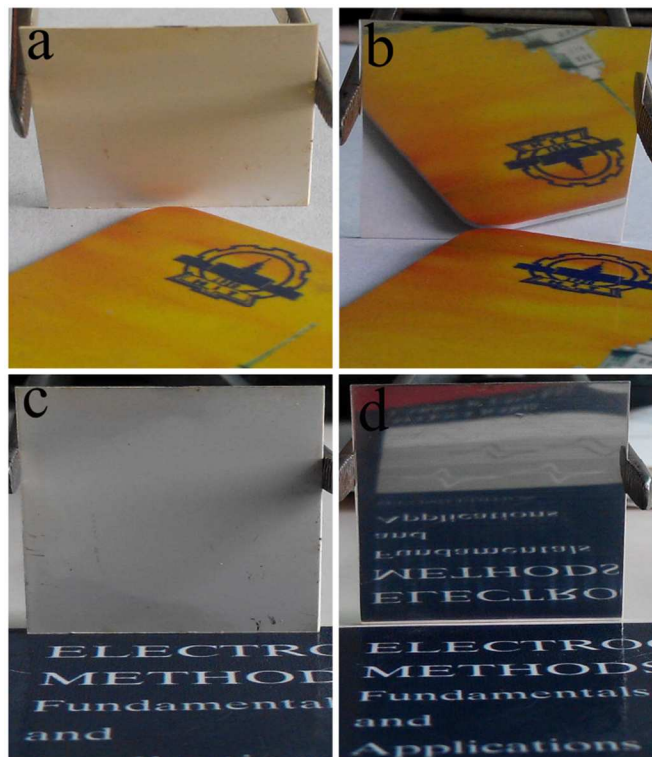


Fig. 1 Macroscopic images of silver deposits obtained from different cyanide-free bath, (a) and (c) without additive, (b) and (d) with additive.

Clearly, silver deposits in Fig 1 (a) and (c) obtained from the cyanide-free bath without additive are white with relatively rough surface. Contrastingly, with the addition of the composite additive into the bath, smooth and compact silver deposits with mirror brightness were obtained as displayed in Fig. 1 (b) and (d). This indicates that the introduced composite additive is effective to significantly improve the appearance of the silver

deposit, which can meet the request of application in decorative purposes.

SEM and AFM were employed to characterize the surface morphology and roughness of the silver deposits. Fig. 2 displays SEM top view images of the silver deposits obtained from the cyanide-free bath with and without additive.

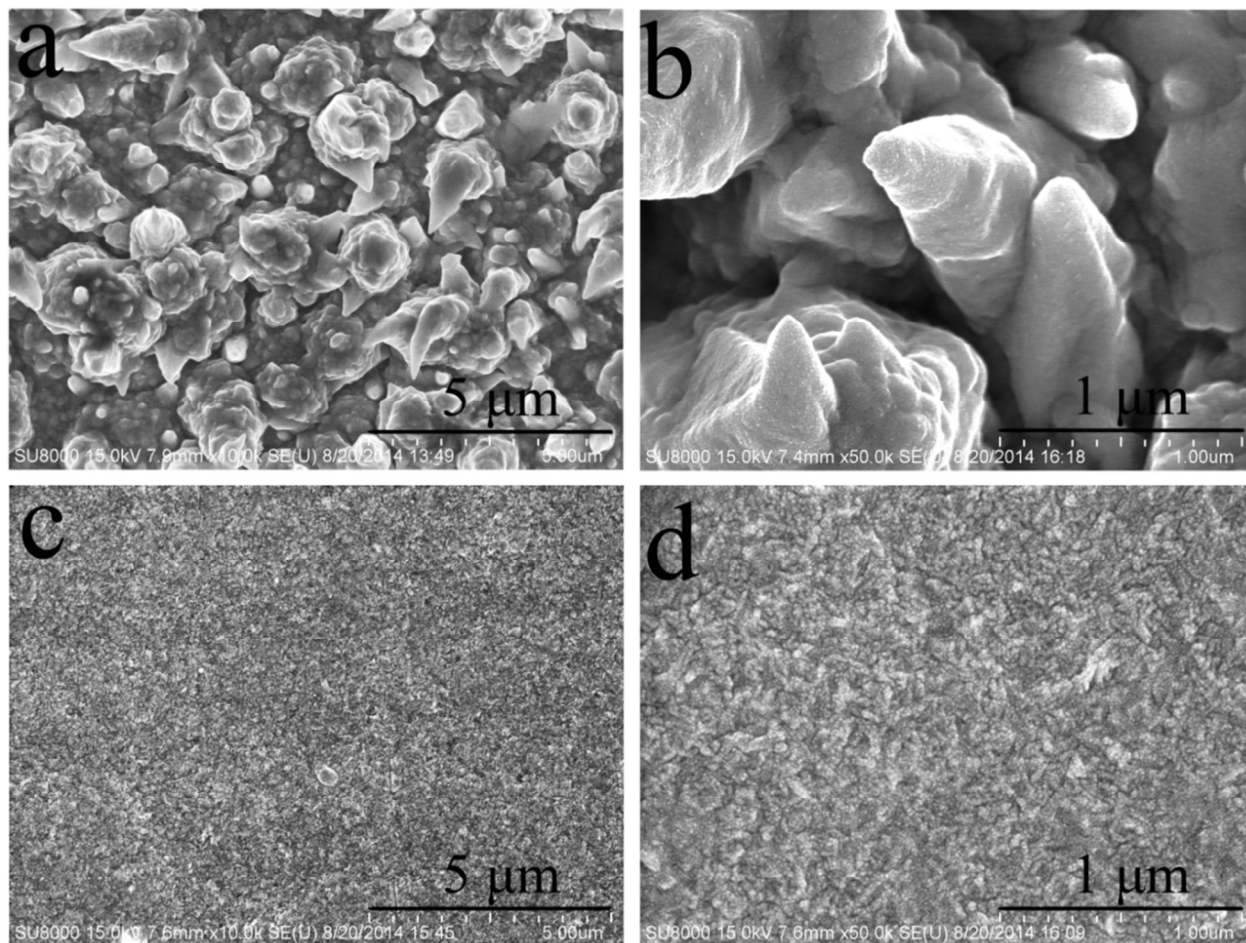


Fig. 2 SEM images of the top views of silver deposits obtained from silver electroplating bath (a) and (b) without additive, (c) and (d) with additive.

Fig. 2 (c) and 2(d) revealed that the silver deposit obtained from the bath with additive was smooth and compact. While from the basic bath without the addition of the composite additive, the silver deposit was much rougher with much bigger grains as displayed in Fig. 2 (a) and 2(b). It can be clearly seen that the corresponding grain size of the silver deposit obtained from the bath with additive was less than that from the basic bath. The deposit obtained from the cyanide-free silver plating bath is pure silver and the purity of the silver deposit was very high as showed in the EDS patterns (Fig.S1, ESI†).

Besides the crystalline structure, the surface roughness of silver deposit or other materials is also a key consideration for industrial applications.²⁰ AFM three-dimensional height images of silver deposits obtained from the cyanide-free bath without and with additive are used to demonstrate the surface roughness as presented in Fig. 3(a) and 3(b), respectively.

As shown in Fig. 3(a), large crystal grains exist on the silver deposit obtained from the basic bath. Compared to that from the

basic bath, the silver deposit in Fig. 3(b) from the bath with additive showed had a smoother morphology with smaller crystal grains. The R_a , R_q and R_{max} of the silver deposit obtained from the basic bath were 137.00 nm, 176.00 nm and 1055.00 nm, respectively. Contrastingly, the R_a , R_q and R_{max} of the silver deposit in Fig. 3(b) were 6.73 nm, 8.70 nm and 56.8 nm, respectively. It can therefore be concluded from the SEM and AFM images that the investigated cyanide-free silver plating bath possessed excellent levelling capacity with the addition of the composite additive into the bath. As displayed in the XRD patterns, with the addition of the introduced additive into the cyanide-free silver plating bath the grain sizes of the silver deposits are much smaller, corresponding to the results of SEM and AFM measurements (Fig.S2, ESI†).

The cathodic polarization curves were measured to investigate the influences and mechanism of the introduced composite additive on electrochemical behaviors in the silver plating baths. Fig. 4 displays the cathodic polarization curves of the bath without and with additive.

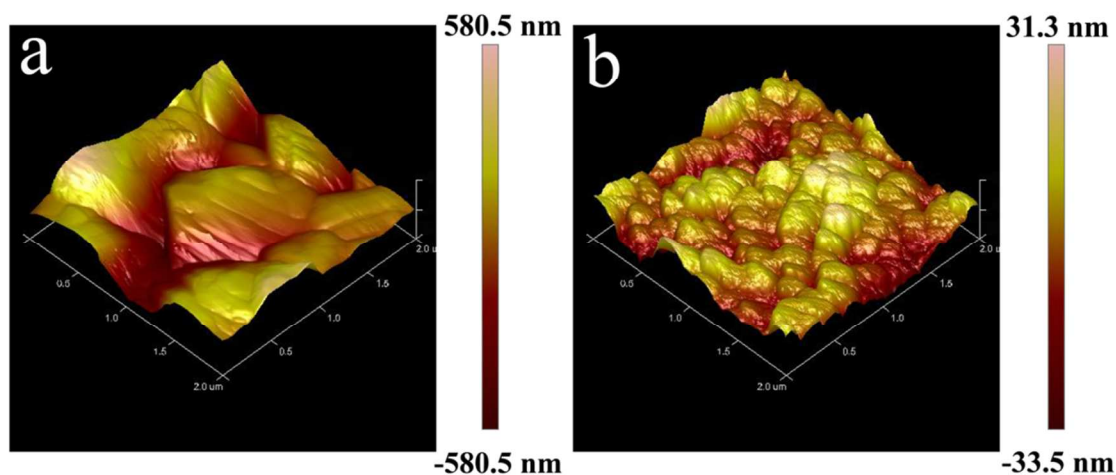


Fig. 3 AFM three-dimensional height images of silver deposits obtained from silver electroplating bath (a) without additive and (b) with additive.

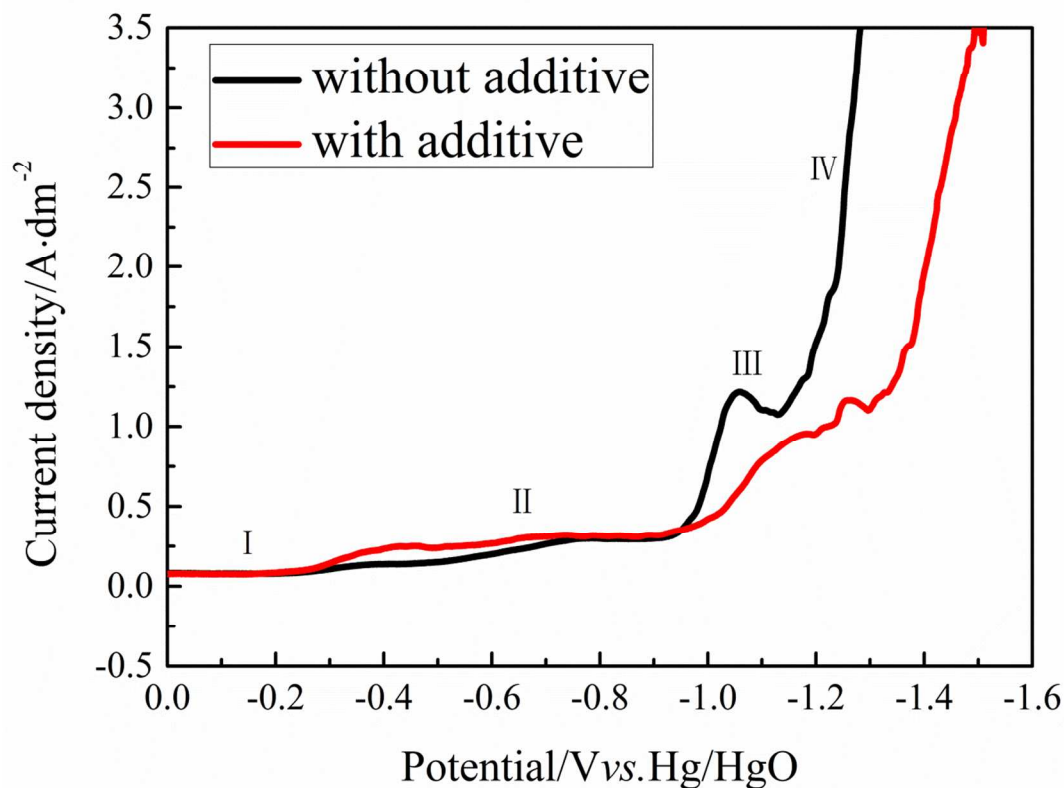


Fig. 4 Cathodic polarization curves of the glass carbon electrode in silver electroplating baths without additive and with additive.

Both curves in Fig. 4 have four parts: I with nonsignificant current density corresponding to the overpotential, II with a rising current attributed to electrodeposition of silver, III with a platform in accord with the limit current density resulted from the diffusion of the electroactive substances, and IV with a sharply rising caused by hydrogen evolution. The curve from the bath with the additive has a bigger overpotential and lower corresponding current density than that from the bath without additive. The utilization of additives can increase the cathodic polarization and resulted in smaller grains because no solvent degradation or dendritical crystal appears during

silver deposition at bigger overpotential. This indicates that the addition of the additive inhibited the electrodeposition process. Thereby tiny silver particles can be obtained to refine the crystalline structure and get fine grains by promoting the bigger cathodic polarization, which agrees with the results of the macroscopic appearance and microscopic morphology (SEM and AFM images) as well as the X-ray diffraction (XRD) patterns displayed in Fig.S2 of electronic supplementary information.

In summary, we report an effective additive used for a new

cyanide-free silver electroplating bath. With the addition of the composite additive into the investigated cyanide-free silver plating bath, smooth and compact silver deposit with mirror brightness and smaller grains was obtained. SEM and AFM images confirm that mirror bright silver deposit with excellent leveling capability and smooth and compact morphology could be electrodeposited from the investigated cyanide-free bath with the introduced composite additive. The cathodic polarization curves demonstrated that the introduced composite additive improves the performance of the silver deposit and refine the crystalline structure by inhibiting the electrodeposition process and causing a bigger overpotential as well as lower corresponding current density.

Experimental section

Silver electroplating experiments were conducted under galvanostatic conditions in a cell employing the copper sheet as the cathodic substrate. The silver plating bath was prepared firstly by adding 0.09 M AgNO₃ into a solution containing 0.7 M DMH, 0.7 M NA, and 0.7 M K₂CO₃. The pH value of the bath was then adjusted to 10.0~14.0 with KOH solution. Lastly, the composite additive was added into the prepared bath.

The electrochemical measurements were performed in a three-electrode cell at 328 K. A glassy carbon electrode (GCE) with a diameter of 3 mm was employed as the working electrode (WE). The counter electrode (CE) was a platinum plate and a mercuric oxide electrode (Hg/HgO) was used as the reference electrode (RE). The scanning potential was from 0 V to -1.6 V with a sweep rate of 1 mV/s.

Field emission scanning electron microscopy (FE-SEM, Hitachi SU8000) was employed to characterize the surface morphologies and the composition of the silver deposits obtained from the cyanide-free bath with and without additive. Atomic force microscope (AFM) was used to reveal the leveling capability of the bath and the surface roughness of the silver deposits. AFM analysis was carried out with a Dimension Icon (Bruker), working in contact mode with the silicon nitride cantilever. The crystalline structure of the silver deposits was characterized by XRD analysis with a D/max-3C x-ray diffractometer at a scanning rate of 0.02°/s with Cu K_α radiation.

Acknowledgements

Financial support from the State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (2012DX03) for this work is gratefully acknowledged.

Notes and references

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† Electronic Supplementary Information (ESI) available: The EDS and XRD patterns of silver deposit, obtained from the bath without and with

the introduced composite additive, as well as the copper substrate. See DOI: 10.1039/c000000x/

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