

2009-08-28

Ellipsometric Study on Colored Electroplating of Cuprous Oxide on Ni Substrate

Xue-song FENG

Jing-lei LEI

Ai-xiang CHEN

Wan-shan YIN

Ling-jie LI

Sha ZHENG

Hui ZHAO

See next page for additional authors

Recommended Citation

Xue-song FENG, Jing-lei LEI, Ai-xiang CHEN, Wan-shan YIN, Ling-jie LI, Sha ZHENG, Hui ZHAO, Shao-yan PAN. Ellipsometric Study on Colored Electroplating of Cuprous Oxide on Ni Substrate[J]. *Journal of Electrochemistry*, 2009 , 15(3): 310-314.

DOI: 10.61558/2993-074X.2001

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol15/iss3/15>

This Article is brought to you for free and open access by Journal of Electrochemistry. It has been accepted for inclusion in Journal of Electrochemistry by an authorized editor of Journal of Electrochemistry.

Ellipsometric Study on Colored Electroplating of Cuprous Oxide on Ni Substrate

Authors

Xue-song FENG, Jing-lei LEI, Ai-xiang CHEN, Wan-shan YIN, Ling-jie LI, Sha ZHENG, Hui ZHAO, and Shao-yan PAN

Corresponding Author(s)

镍基彩色电沉积 Cu_2O 椭圆偏振光谱研究封雪松^{1,2}, 雷惊雷^{1*}, 陈爱祥¹, 阴宛珊¹, 李凌杰¹,
郑莎¹, 赵辉¹, 潘少彦¹

(1 重庆大学化学化工学院, 重庆 400044; 2 四川理工学院材料与化学工程学院, 四川 自贡 643000)

摘要: 应用电化学方法在 Ni 基底上沉积 Cu_2O 彩色膜层以期提高装饰效果. X 光电子能谱 (XPS)、扫描电子显微镜 (SEM) 和能量色散谱 (EDS) 测试表明, 膜层由 Cu_2O 组成, 沉积层光滑平整, 且 Cu_2O 层均匀覆盖 Ni 基底. 椭圆偏振光谱表征不同沉积时间的膜层, 提出膜层内存在由 Ni 逐渐变为 Cu_2O 的过渡层, 建立“空气— Cu_2O 层—过渡层—Ni 基底”4 层膜模型, 并借助梯度有效介质近似解析椭圆偏振光谱, 得到不同沉积时间的膜层厚度以及厚度随时间线性增长关系.

关键词: 表面处理; 彩色电沉积; Cu_2O ; 椭圆偏振光谱法; 有效介质近似

中图分类号: O646.541

文献标识码: A

电镀 Ni 结晶细致, 耐磨性好, 易得镜面光泽镀层, 但 Ni 呈银白色, 色彩单调, 可再镀 Cu 着色. 电化学着色方法是在基底上沉积一定厚度的氧化物膜层或盐膜层, 由光的干涉作用而显色^[1]. 颜色主要决定于沉积膜层的组成及厚度. 受电沉积过程中物质浓度、pH 值、温度、电流密度以及沉积时间等条件制约, 镀层色彩不易重现且色泽不匀^[2]. 目前针对上述不足已有不少研究^[3-6], 但尚未充分认识精确控制沉积膜层厚度的重要性.

若应用反射式椭圆偏振光谱分析光学参量 Δ 和 Ψ , 得知椭圆偏振光被膜层反射后偏振状态的改变, 可确定膜层光学常数 (折射系数 n 吸光系数 k) 和厚度^[7-9]. 本文借助反射式椭圆偏振光谱精确测定 Ni 基底上 Cu 彩色沉积层的厚度, 研究沉积层厚度随电沉积时间的变化规律, 可深入了解 Ni 基电化学着色机理, 优化电化学着色工艺.

1 实验

普通碳钢片 (2.0 cm × 2.0 cm × 0.1 cm) 作基片, 依次以 200、400、800、1200 号砂纸逐级打磨至镜面, 水洗、除油、活化、镀光亮 Ni (普通 Watt 槽, 电流密度 1.00 A/dm², 45.0 °C, 25 min)、水洗、活化、电化学着色 (镀液 CuSO_4 37 g/L, NaOH 45 g/L

食糖 90 g/L, 37.0 °C, 恒电流).

使用 M2000U 椭圆偏振光谱仪 (美国 J. A. Woollam) 作反射式椭圆偏振光谱测量, 波长 600 ~ 1000 nm, 入射角 70°, 数据解析采用仪器自带 WVASE32 程序.

使用带能量色散谱 (EDS) 探头的 VEGA II LMU 扫描电子显微镜 (SEM, 捷克 TESCAN) 观察样品形貌、分析表面元素.

使用 ESCALAB250 光电子能谱仪 (XPS 美国 Thermo Fisher Scientific) 测定元素价态.

2 结果与讨论

2.1 SEM 及 EDS

实验表明, 在电流密度 0.04 ~ 0.16 A/dm², 沉积时间 300 s 内, Ni 基电沉积 Cu_2O 层颜色随时间由“金黄 → 紫 → 蓝 → 绿 → 金黄”顺序循环改变, 色泽均匀鲜艳. 图 1 为光亮 Ni 基底 (a) 及其着色样品 (b) (电流密度 0.16 A/dm², 沉积时间 120 s) 的 SEM 照片. 总体上, 光亮 Ni 镀层及着色层表面均很平整, 但 Ni 镀层有少量针孔.

根据 EDS 分析, 图 2 示出对应于图 1b 样品内 Ni (a) 和 Cu (b) 的元素分布 (图中黑点), 可以发

现, Ni和 Cu分布十分均匀, 并且可认定着色层均匀覆盖光亮 Ni基底. EDS进一步分析表明, 该膜层表面主要含 Ni(84.36%), Cu(6.48%), O(4.03%), Fe(2.62%)以及 C(2.51%)等元素. 其中 Fe、N 分别来自于基底和 Ni层, Cu来自着色

层. 另据 XPS实验(图 3), 沉积层中 Cu元素 $2\text{P}_{3/2}$ 及 $2\text{P}_{1/2}$ 峰位置和 CuLM2俄歇峰位分别为 932.6、952.4和 916.3 eV, 表明电沉积产物成分主要为 Cu_2O ^[10].

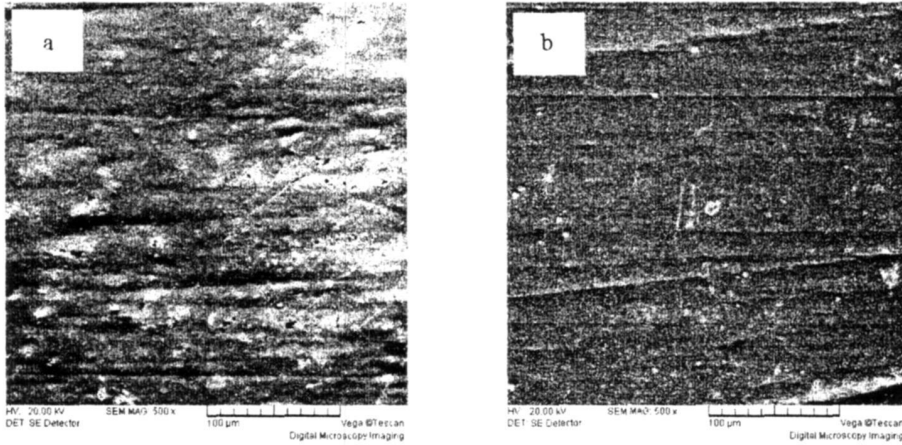


图 1 Ni层 (a)和电沉积 Cu_2O 着色层 (b)SEM 照片

Fig 1 SEM images of the Ni substrate (a) and colored electroplating Cu_2O coating (b)

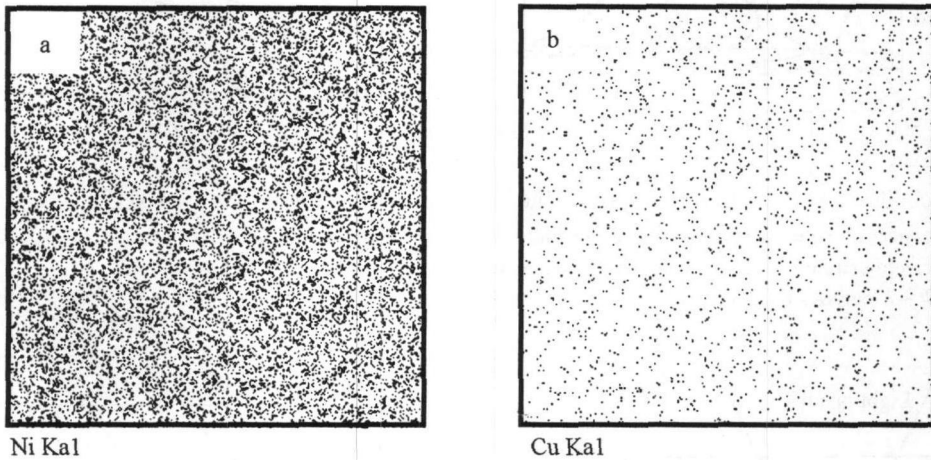


图 2 Ni基 Cu_2O 着色层 (见图 1b样品)内 Ni(a)和 Cu(b)元素分布 (图中黑点)

Fig 2 Ni(a) and Cu (b) element mapping distribution (shown as dots) for the colored electroplating coating of Cu_2O on Ni substrate (sample as Fig 1b)

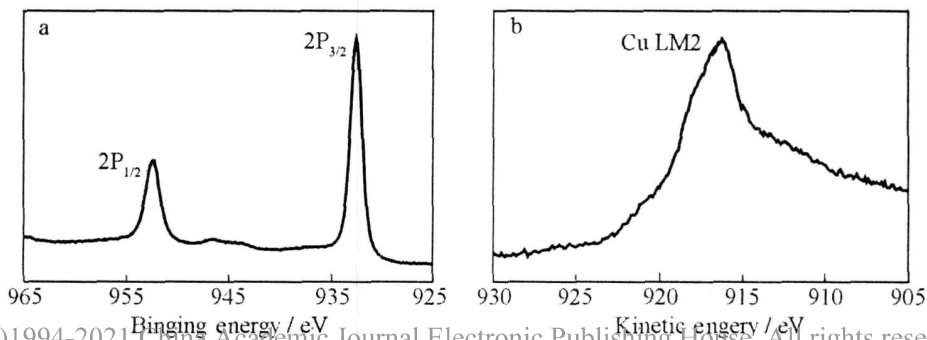


图 3 Ni基 Cu_2O 着色层的 XPS谱图 a Cu 2p 峰; b 俄歇峰

Fig 3 XPS patterns for the colored electroplating coating of Cu_2O on Ni substrate a Cu 2p scan b Auger line

2.2 反射式椭圆偏振测试

在 0.09 A/dm^2 电流密度下, 每 30 s 记录样品颜色 (见表 1), 由反射式椭圆偏振光谱检测样品光学参量 Δ 和 Ψ 随波长 λ 的改变 (如图 4). 依据“环境-膜层-基底”3层膜模型^[7]构建“空气-Cu₂O层-Ni基底”光学模型 (图 5a). 计算表明,

此模型不能很好符合实验结果, 例如表 1 中 2 样品 (沉积时间为 90 s), 其理论 $\Psi \sim \lambda$ 曲线 (图 6a 实线) 与实验曲线 (图中离散点) 仅变化趋势相近. 这可能是 3 层膜模型较粗糙, 只反映了体系的主要特征而没体现更多细节.

表 1 Ni 基 Cu₂O 着色层颜色随沉积时间的变化

Tab 1 Variation of color with electroplating time for the electroplating coating of Cu₂O on Ni substrate

No	1	2	3	4	5	6
Electroplating time/s	60	90	120	150	180	210
Color	Yellow green	Gold	Purplish red	Emerald	Purplish red	Dark green

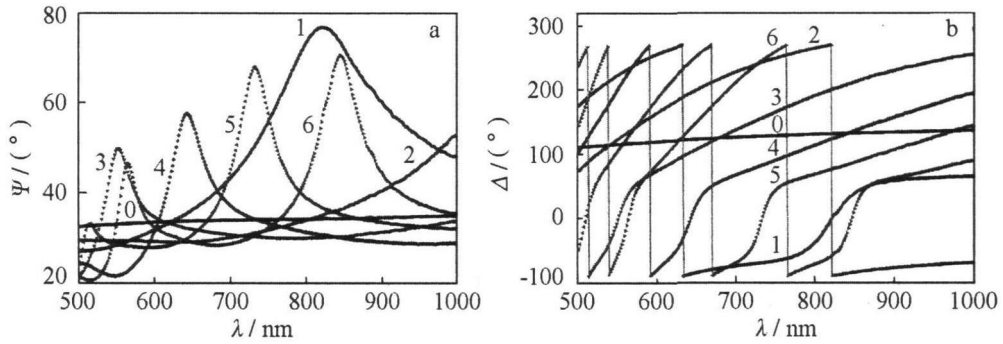


图 4 不同沉积时间 Ni 基 Cu₂O 着色层的椭圆偏振实验结果 a $\Psi \sim \lambda$ 曲线, b $\Delta \sim \lambda$ 曲线

Fig 4 Ellipsometric experimental data corresponding to different electroplating times (0~6/s, 0, 60, 90, 120, 150, 180) for the electroplating coating of Cu₂O on Ni substrate a $\Psi \sim \lambda$ curves b $\Delta \sim \lambda$ curves

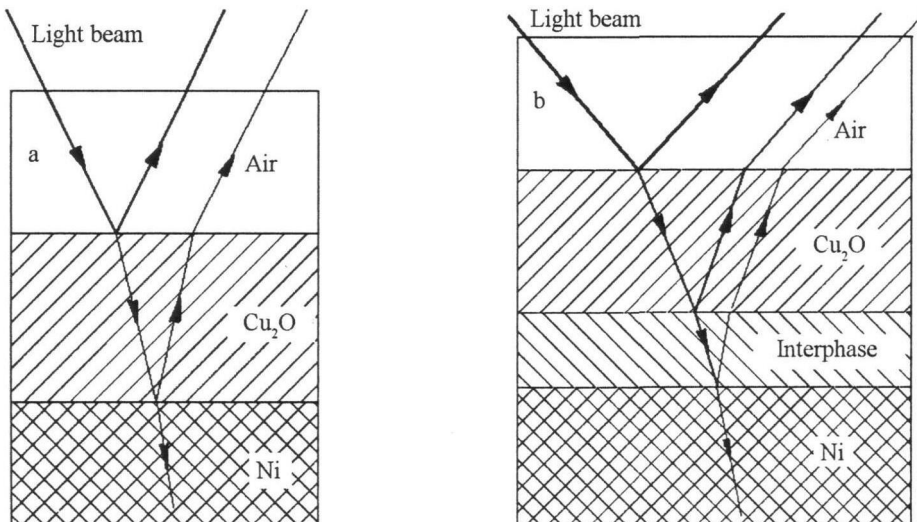


图 5 椭圆偏振光谱 3 层膜 (a) 及 4 层膜 (b) 光学模型

Fig 5 3-layer (a) and 4-layer (b) optical models for deconvoluting ellipsometric data

若考虑 Ni 基底的微观不平整性, Ni 基底与 Cu_2O 间可能存在一层较薄的过渡层, 其组成由 Ni 逐渐变化为 Cu_2O , 则上述光学模型需修正为“空气- Cu_2O 层-过渡层-Ni 基底”4 层膜模型(图 5b). 借助梯度膜模型模拟过渡层内 Ni 含量的逐渐改变(由 100% 至 0), 并应用有效介质近似 (Effective Medium Approximation, 简称 EMA)^[8-9] 计算过渡层的光学常数, 4 层膜模型可较好地解析椭圆偏振实验数据(6 个样品, 见表 2). 图 6 给出沉积时间为 90 s (表 2 中 2# 样品) 的理论 $\Psi \sim \lambda$ (a) 和 $\Delta \sim \lambda$ (b) 曲线(图中虚线), 可见其与实验数据(图中离散点)符合较好. 另外, 尝试以 Cu 层或 CuO 层代替 Cu_2O 层的多个光学模型, 都不能与实验数据符合, 进一步表明彩色沉积层的主要组成确实为 Cu_2O .

以膜的总厚度 T_{total} (过渡层与 Cu_2O 层厚度之和) 对沉积时间 t 作图, 得出沉积层总厚度随时间线性增长, 其线性方程为:

$$T_{\text{total}} = 1.135t - 4.429 \quad (R^2 = 0.994)$$

据此, 即可由沉积时间及电流效率计算相应的膜层厚度, 继而依据薄膜干涉以及色度学^[11-12] 原理预测膜的颜色变化, 确定颜色与膜厚度的对应关系, 再由膜厚增长公式计算某一特定颜色所需要的沉积时间, 从而可在工艺上实现膜颜色的精确控制.

3 结 论

电沉积 Cu 对 Ni 基底着色, 着色层主要成分为分布均匀的 Cu_2O ; 借助组成逐渐变化的有效介质

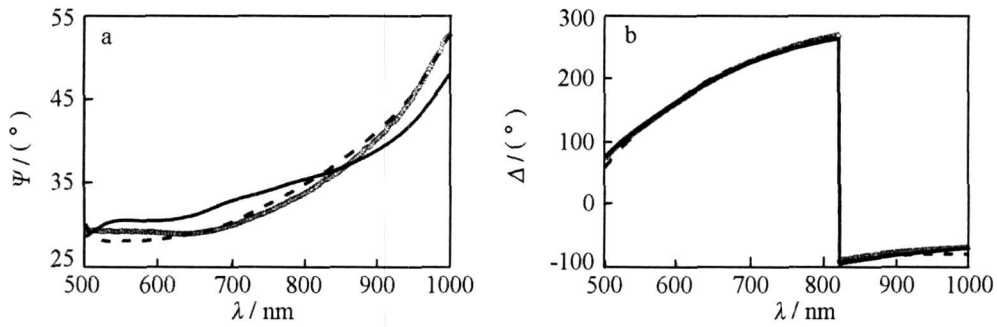


图 6 2# 样品理论(实线: 3 层膜模型, 虚线: 4 层膜模型)曲线与实验曲线(离散点)
a $\Psi \sim \lambda$ 曲线, b $\Delta \sim \lambda$ 曲线(3 条 $\Delta \sim \lambda$ 曲线几乎重合)

Fig 6 Experimental data and fitted curves (solid: 3-layer model dash: 4-layer model) of the 2# sample
a $\Psi \sim \lambda$ curves b $\Delta \sim \lambda$ curves the three $\Delta \sim \lambda$ curves in (b) are almost overlapped

表 2 由椭圆偏振光谱数据计算的不同沉积时间的 Ni 基 Cu_2O 着色层厚度

Tab 2 Coating thickness of Cu_2O on Ni substrate corresponding to various electroplating time calculated from ellipsometric data

No	Electroplating time /s	Thickness/nm		
		Interphase	Cu_2O layer	Total
1	60	15.33	62.70	78.03
2	90	15.79	97.41	113.20
3	120	19.25	135.37	154.62
4	150	20.07	164.10	184.17
5	180	19.92	211.28	231.20
6	210	24.89	252.62	277.51

光学模型,很好解析着色层的椭圆偏振光谱并精确求得着色层厚度,发现沉积速率与时间成正比.

致谢:本研究工作得到了重庆大学大型仪器设备开放基金项目资助,特此感谢!

参考文献 (References):

[1] WU Tian-cai (吴天才). Electroplating of colored films [J]. Electroplating and Finishing (in Chinese), 1994, 13(2): 1-4.

[2] HE Sheng-long (何生龙). Techniques of colored electroplating [M]. Beijing: Chemical Industry Press 2007. 4.

[3] WANG Quan-fa (汪泉发). Electrolytic coloring of copper [J]. Electroplating and Pollution Control (in Chinese), 1988, 8(5): 10-11.

[4] XU Shu-kai (许书楷), YANG Fang-zu (杨防祖), GE Fu-yun (葛福云), et al Prepare and structure of electrodeposited color chromium coatings [J]. Electroplating and Pollution Control (in Chinese), 1992, 11(6): 13-17.

[5] ZHENG Fu-yang (郑辅养), MA Ting-chun (马廷椿), WEN Guo-mou (温国谋). Coloring of plating copper [J]. Materials Protection (in Chinese), 1997, 30(9): 18-19.

[6] LUN Chun-hui (栾春晖), XUE Yong-qiang (薛永

强), HAN Xiu-juan (韩秀娟). Molybdate electrolytic coloring on nickel coating [J]. Materials Protection (in Chinese), 1999, 32(8): 11-13.

[7] Azzam R M A, Bashara N M. Ellipsometry and polarized light [M]. Amsterdam: North Holland Publishing Comp 1977. 283.

[8] Aspnes D E, Kinsbron E, Bacon D D. Optical properties of Au: sample effects [J]. Physical Review B, 1980, 21(8): 3290-3299.

[9] LEI Jing-lei (雷惊雷), LI Ling-jie (李凌杰), ZHANG Sheng-tao (张胜涛), et al Studies on corrosion behavior of copper electrode in weak alkaline solution [J]. Acta Chimica Sinica (in Chinese), 2001, 59(8): 1216-1221.

[10] WANG Jian-qi (王建琪), WU Wen-hui (吴文辉), FENG Da-ming (冯大明). Introduction on XPS/XAES/UPS [M]. Shanghai: National Defense Industry Press 1992. 530.

[11] MU Guo-guang (母国光), ZHAN Yuan-ling (战元龄). Optics [M]. Beijing: Peoples' Education Press 1979. 190.

[12] QI Tong-fei (戚同非), WU Yong-gang (吴永刚), LIN Xiao-yan (林小燕), et al Computer simulation for change of reflected color in film thickness control process [J]. Vacuum (in Chinese), 2005, 42(1): 28-32.

Ellipsometric Study on Colored Electroplating of Cuprous Oxide on Ni Substrate

FENG Xue-song^{1,2}, LEI Jing-lei^{1*}, CHEN Ai-xiang¹, YIN Wan-shan¹, LI Ling-jie¹, ZHENG Sha¹, ZHAO Hui¹, PAN Shao-yan¹

(1. College of Chemistry and Chemical Engineering Chongqing University, Chongqing 400044, China;

2. Department of Material and Chemical Engineering Sichuan University of Science and Engineering Zigong 643000, Sichuan, China)

Abstract: The colored Cu₂O coating was electroplated on Ni substrate to meet the decorative requirements. Results of X-ray photoelectron spectroscopy (XPS) indicate the coating consisting of Cu₂O. Images of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) show that the Cu₂O coating is smooth and uniform, and covers the Ni substrate wholly. Ellipsometric measurements for Cu₂O coatings with various electroplating time were carried out. Using a 4-layer model of "Air-Cu₂O layer-interphase Ni", the interphase was modeled with the graded effective medium approximation (EMA), the ellipsometric data were deconvoluted and the Cu₂O coatings thickness of Cu₂O was obtained. Results reveal that the Cu₂O coating thickness increases linearly with the electroplating time.

Key words: surface treatment; colored electroplating; cuprous oxide; ellipsometry; effective medium approximation