Asian Journal of Chemistry; Vol. 31, No. 4 (2019), 891-895

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21823

Effect of Additives on Electrodeposition of Zinc-Nickel Alloy On Mild Steel

DINESH KUMAR CHELIKE and K. JULIET GNANA SUNDARI*

Department of Chemistry, Karunya Institute of Technology and Sciences (Deemed to be University), Coimbatore-641114, India

*Corresponding author: E-mail: juliemoses@yahoo.com

Received: 19 November 2018; *Accepted*: 3 January 2019; *Published online*: 27 February 2019; AJC-19303

Considering the good corrosion resistance of Zn-Ni alloy, it is selected in the present study to be the protective coating on mild steel and it is considered as a strong candidate for the replacement of environmentally hazardous cadmium. Zn-Ni alloy coating is applied by electrodeposition at optimum temperature, current density and time. The bath solution used is consisting of EDTA as complexing agent. The electrodeposition is also carried out with tartaric acid and benzaldehyde additives to have good corrosion resistance and brightness. The electrodeposits obtained with and without additives are examined for nature and alloy composition. The corrosion behaviour of the electrodeposits is studied by Tafel polarization and electrochemical impedance spectroscopy.

Keywords: Electrodeposition, Zn-Ni alloy, EDTA, Electrochemical techniques, Additives.

INTRODUCTION

In the present world, the loss due to corrosion is enormous. Since metals are widely used in engineering field, much attention is given to corrosion control. One of the methods of controlling corrosion on metallic surface is applying protective coatings [1]. Mild steel is one of the least expensive steels; which exhibits the favourable properties such as high hardness, easy weldability, and good durability. These properties allow for the passage of electric current throughout the metal without distortion. When mild steel is handled under acids, alkalis and salt solutions in various industrial processes under the conditions of chlorides, sulphates and nitrates it causes corrosion. As steel is used for many engineering applications it should be sealed with a protective coating to avoid corrosion [2].

Galvanizing is most widely used metallic coating method for corrosion protection, which involves the application of metallic zinc. Zinc can give good corrosion protection to steel surface but the corrosion resistance of zinc alloy coating has greater efficiency than zinc coating. The alloy coatings exhibit good corrosion resistance towards oxidizing agents and also towards aggressive high temperature corrosive environments which makes them to use in major industries like automotive, aircraft and in machinery parts. Zinc can be alloyed with metals like nickel, cobalt, copper, aluminium, molybdenum, *etc*. for the replacement of environmentally hazardous cadmium. The use of corrosion inhibitors is the most convenient and practical method to protect the metals from attack of corrosion [3]. Most of the inhibitors are organic species, that are called as brighteners or grain refiners, which help in attaining uniform, smooth and homogenous deposits.

In the present study, Zn-Ni alloy is electroplated on mild steel by electroplating technique [4-6]. Electroplating is the technique used for applying protective coating and it is a process using electrical current to reduce cations of a desired material from a solution and coat that material as a thin layer onto a conductive substrate surface [7]. The additives like benzaldehyde and tartaric acid are employed in the electrolytic bath containing EDTA as the complexing agent and the effect of additives on the nature of electrodeposit is discussed. Smooth and defect-free deposit can be obtained by the addition of benzaldehyde and it is exhibiting high corrosion resistance. Addition of tartaric acid has an appreciably positive effect in hindering the oxidation process thereby it can prevent corrosion on metallic surface [8].

EXPERIMENTAL

The electrodeposition of Zn-Ni alloy coatings onto mild steel was conducted by galvanostatic electrodeposition [9,10] at roomtemperature and current density of 1 A/dm^2 for 30 min.

The bath solution was prepared using analytical grade chemicals with double distilled water which consisted EDTA as complexing agent and the bath solution was prepared by mixing the chemicals as given in Table-1. The concentration of zinc and nickel in the bath solution were 0.25 and 0.75 g/L, respectively.

TABLE-1
BATH COMPPOSITION AND OPERATING CONDITIONS

Constituents present in the bath	Amount (g/L)	Operating conditions
ZnO	90	Temperature 27 °C
NaOH	90	Current density 1 A/dm^2
$NiSO_4$	15	pH 11
EDTA	15	Deposition time 30 min
Benzaldehyde	0.25 to 0.75	Anode zinc
Tartaric acid	0.25 to 0.75	Cathode mild steel

Electrodeposition with and without additives: Electrodeposition was carried out by employing a two electrode system, containing zinc (2.5 cm × 2.5 cm) as anode and mild steel plate of dimension (7.5 cm × 2.5 cm) were used as cathodic substrates. Surface of mild steel plate and zinc anode were cleaned with emery paper, immersed in 5 % H_2SO_4 and washed with deionized water. Then the surface of mild steel was wiped with cotton to remove the loosely adhered particles, ultrasonically degreased with acetone for about 15 min and then mechanically polished to attain mirror finish. The electrodes were immersed in the beaker containing the bath solution and the distance between mild steel and zinc plate was about 2.5 cm.

The electrodeposition was carried out with Zn-Ni alloy at 1 A/dm^2 current density using DC power supply unit and a multimeter for 30 min. After deposition the plates were rinsed well to remove the loosely absorbed oxide particles and left for air drying. The deposited mild steel was removed, washed immediately with deionized water, dried and weighed from which the weight of electrodeposition was calculated. Electrodeposition was also carried out with tartaric acid and benzaldehyde as additives with the concentrations as 0.25, 0.50 and 0.75 g/L at the same operating conditions. After 30 min, the coated mild steel was removed and washed immediately with deionized water, dried and weighed.

Characterization of deposited mild steel: The electrodeposited mild steel plates in the presence and absence of additives were examined for the nature, alloy composition and the surface morphology of the electrodeposit was studied by scanning electron microscopy (SEM). From the XRD patterns of Zn-Ni alloy electrodeposits recorded with and without additives using Cu/K_α radiation by an X-ray diffractometer model. Crystallite size is determined using Debye Scherrer equation. Corrosion behaviour of electrodeposits prepared are examined by electrochemical methods such as Tafel polarization and electrochemical impedance spectroscopy (EIS) techniques and the characteristics of electrodeposits with benzaldehyde and tartaric acid are compared. The weight loss method was used to assess the corrosion of electrodeposited mild steel samples in 0.05 M H_2SO_4. The coated samples were suspended in the apparatus for complete immersion in 0.05 M H_2SO_4 and the exposure was observed for 24 h while the weight loss measurements took place using the electronic digital weighing balance.

RESULTS AND DISCUSSION

Alloy composition: Composition of alloy electrodeposits prepared at optimized condition in the presence and absence of additives were analyzed by atomic absorption spectroscopy and the results are presented in Table-2. The high zinc content of the alloy is apparently due to the inhibition of Ni^{2+} discharge by the surface $Zn(OH)_2$ precipitated when hydrogen evolution caused local surface pH to rise. The charging process of alkaline zinc secondary batteries is accompanied by the formation of hydrogen, the rate of hydrogen evolution on zinc and corrosion rate of zinc in alkali. The predominant solution species has been represented as tetrahedral $Zn(OH)_4^{2-}$ ions.

$$Zn + OH^- \longrightarrow ZnOH + e^-$$

$$ZnOH + OH^- \longrightarrow Zn(OH)_2^- + e^-$$

$$Zn(OH)_2^- + OH^- \longrightarrow Zn(OH)_3^{2-} + e^-$$

$$Zn(OH)_3^{2-} + OH^- \longrightarrow Zn(OH)_4^{2-}$$

TABLE-2
ALLOY COMPOSITION OF Zn-Ni ALLOY ELECTRODEPOSITS WITH AND WITHOUT ADDITIVES

Sample	Composition (%)	
	Zinc	Nickel
Without additive	81.8	10.1
Tartaric acid	82.5	9.9
Benzaldehyde	85.0	9.7

The composition and properties of deposit are influenced by the several factors which affect the hydrogen evolution and hydroxide precipitation. Increase in hydrogen evolution has resulted in increased surface alkylation which leads to greater formation of $Zn(OH)_2$ and inhibition of nickel deposition [11].

X-Ray diffraction: XRD patterns derived for Zn-Ni electrodepositsand that of electrodeposit with tartaric acid and benzaldehyde additives are depicted in Fig. 1. The crystalline size is determined from the measurements of the peak width at half of the maximum peak intensity using Debye Scherrer equation. According to the patterns, the decrease in absorption intensity of diffraction peaks implies that the regular growth of crystallites is hindered due to incorporated additive, providing the free

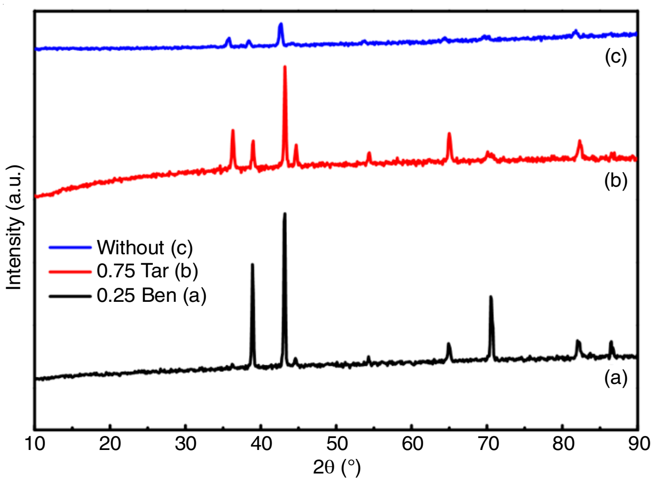

Fig. 1. XRD spectra of Zn-Ni alloy deposit in the absence and presence of additives

energy for the formation of new nucleation sites, which results in high nucleation rate and consequently resulting in fine grained and compact deposits [12]. The peaks at 2θ values of 38°, 42°, 70° and 81°, represent benzaldehyde and tartaric acid (Fig. 1), the broad peak at approximately 42° is attributed to the crystalline nature. This crystallinity results from the super-saturated solution of Zn in Ni matrix as Zn atom occupies Ni atom position within the matrix. The larger crystalline size as given in Table-3 in case of as such deposits without additive may correspond to the grain boundary sites, which are known for the initiation of corrosion [13]. The fine crystalline structure of materials contributes to high enhancement of the localized corrosion resistance. The obtained XRD patterns were compared with the standard JCPDS cards which represented a face centered monoclinic in the absence of additives and monoclinic in the presence of structure.

TABLE-3
CRYSTALLINE SIZE OF THE Zn-Ni ELECTRODEPOSITS IN THE ABSENCE AND PRESENCE OF ADDITIVES

	Crystalline size (nm)
Without additive	0.7530
Tartaric acid	1.6578
Benzaldehyde	1.6558

Scanning electron microscopy (SEM): SEM morphology of electrodeposit obtained with zinc-nickel alloy is shown in Fig. 2, which depicted the presence of small and large crystallites of rectangular and triangle shape densely covering the surface. The surface is smooth, bright and no micro cracks are observed in the micrographs and the size of crystallites is shown in Table-4. The crystallite size of deposit emphasizes that benzaldehyde has small size and the deposit composition depends on the species and composition of electrolytes.

TABLE-4
CRYSTALLITE SIZE OF THE Zn-Ni ELECTRODEPOSITS WITH AND WITHOUT ADDITIVES

Additive	Crystallite size (μm)
Without additive	0.9011
Tartaric acid	1.0563
Benzaldehyde	0.8950

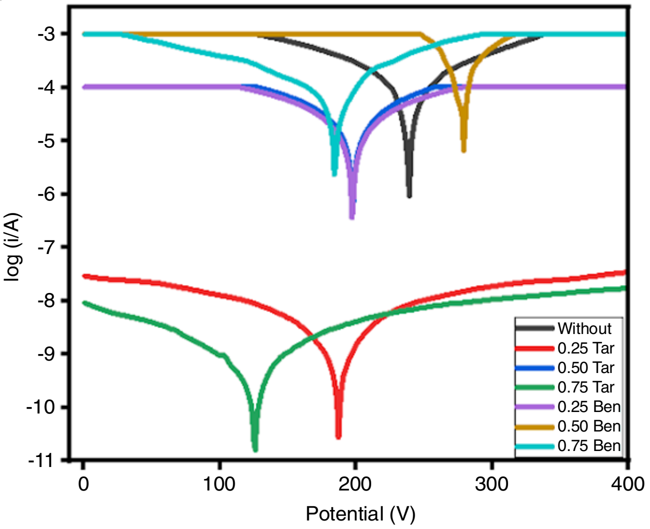

Fig. 3. Tafel polarization curves with and without additives in benzaldehyde and tartaric acid

Tafel polarization: In order to study the behaviour of the coated material during an exposure to a corrosive solution, potentiodynamic polarization measurements were recorded. The Tafel plots (Fig. 3) for the alloy deposits obtained in absence and in presence of different concentrations of benzaldehyde and tartaric acid in the bath recorded in 0.05 M H_2SO_4 medium. The corresponding corrosion current data (I_{corr}) and the calculated corrosion rate (CR) are given in Table-5. It was seen, a low I_{corr} was obtained for the alloy deposits, obtained in the presence of 0.25 to 0.75g/L benzaldehyde in the bath. It was known that corrosion resistance of any alloy depends on the ability to form surface protective film. In the present study a low corrosion current infers that a strong thin barrier layer has been formed on the surface of alloy [14] that reduces the active corrosion sites and makes the deposit more corrosive

TABLE-5
CORROSION RATE CALCULATED FROM TAFEL POLARIZATION CURVE

Conc. of additive (g/L)	I_{corr} (amp.)	I_{corr} (mA)	I_{corr} for the area exposed	Corrosion rate (mm/yr)
Without additive				
	2.012×10^{-4}	0.2012	0.00631	0.92301
Benzaldehyde				
0.25	1.480×10^{-4}	0.4180	0.00464	0.42012
0.50	9.990×10^{-4}	0.9990	0.03136	0.32883
0.75	2.237×10^{-4}	0.2287	0.00702	0.10256
Tartaric acid				
0.25	1.433×10^{-3}	1.4330	0.04499	0.65743
0.50	4.581×10^{-4}	0.4581	0.01438	0.21009
0.75	4.412×10^{-4}	0.4412	0.01385	0.20240

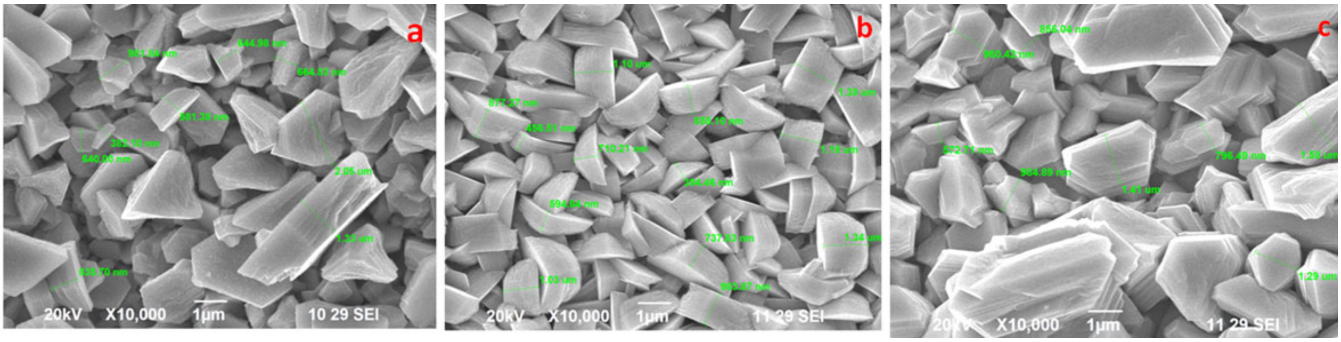

Fig. 2. SEM photograph of the Zn-Ni electrodeposits with (b-c) and without (a) additives

resistance towards sulphate ions. Based on the obtained corrosion current results, corrosion rate was calculated. The Tafel polarization curve depicted that the cathodic curve corresponds to hydrogen evolution and the anodic curve corresponds to metal dissolution, which is one of the key factor for its corrosion resistance property.

Tartaric acid and benzaldehyde added in the bath solution increase the polarization by getting adsorbed on the electrode surface and prevent the corrosion of the electrodeposited alloy. As the concentration of tartaric acid and benzaldehyde increase, the degree of surface coverage increases and the corrosion rate decreases. As aromatic compounds exhibit more corrosion inhibition than aliphatic compounds the corrosion rate of the electrodeposit with benzaldehyde is less than that with tartaric acid. Infact, many organic compounds, above some critical concentration in the plating bath gets decomposed and trapped to the specific parts of the deposits causing hydrogen evolution and thereby increasing the conductive pathways for the corrosive species [15].

Electrochemical impedance spectroscopy: To gain more knowledge on the characteristics of electrochemical process occurring at electrode/electrolyte interface in the corrosive media, EIS measurements were recorded. EIS measurements presented in Table-6 for the alloy coating without and with different concentrations of the additives were represented in the form of Nyquist plots. The Nyquist plots (Fig. 4) displayed in the form of arcs attributed to the charge transfer resistance process at the electrode/electrolyte interface and directly relates to the changes in the coating property [16]. All the plots were acquired at their respective open circuit potentials (OCP) in the respective corrosive medium (0.05M H_2SO_4). The charge-transfer resistance (R_{ct}) values were determined from the difference in impedances at lower and higher frequencies.

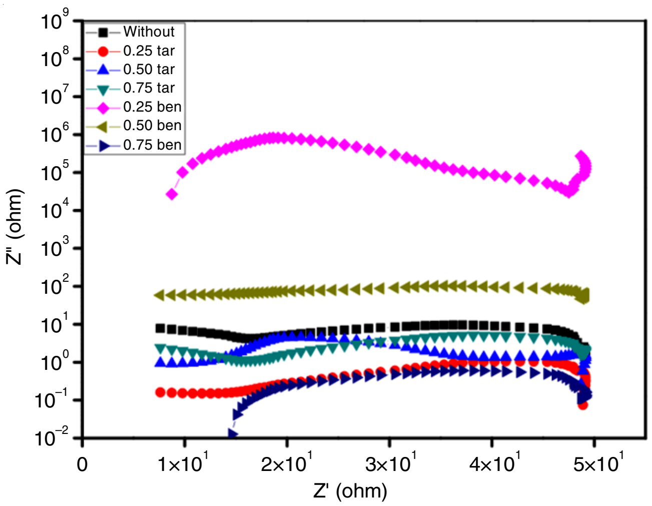

Fig. 4. Impedance spectra with and without additives in benzaldehyde and tartaric acid

Higher R_{ct} values correspond to greater corrosion resistance of the coated system [17]. As shown in Table-6, a higher value of R_{ct} is observed for the deposit obtained from the bath containing benzaldehyde than with tartaric acid and this result indicates that the presence of aldehyde in the bath facilitates the formation of a defect-free deposit and prevents the dissolution of metal in the alloy. Nyquist plots with a depressed semicircle under the real axis at benzaldehyde concentrations other than 0.75g/L revealed the surface heterogeneity caused by surface roughness and porous layers [18]. Good agreement with Tafel and EIS studies is observed from the analysis of the electrodeposits.

TABLE-6
CHARGE TRANSFER RESISTANCE OF THE ELECTRODEPOSITS WITH AND WITHOUT ADDITIVES

Conc. of additives (g/L)	R_{ct} (kΩ)
Without additive	0.489
Benzaldehyde	
0.25	1.446
0.50	1.735
0.75	2.205
Tartaric acid	
0.25	0.257
0.50	0.267
0.75	0.346

Weight loss technique: The weight loss measurements were analyzed for the complete period of one day immersion of the electrodeposits in 0.05M H_2SO_4 and the results are shown in Table-7. The decrease in corrosion rate observed can be attributed to the adsorption of benzaldehyde and tartaric acid on the electrodeposit which displayed a protective layer that slowed down the corrosion rate. From the results, it is revealed that there is comparatively a good agreement with electrochemical measurement.

TABLE-7
CORROSION RATE FROM WEIGHT LOSS TECHNIQUE

Conc. of additives (g/L)	Corrosion rate (mm/yr)
Without additive	1.4231
Benzaldehyde	
0.25	0.5020
0.50	0.2834
0.75	0.1026
Tartaric acid	
0.25	0.7573
0.50	0.3854
0.75	0.2105

Conclusion

Zinc-nickel alloy coatings electrodeposited on mild steel plate was uniform and bright in texture. X-ray diffraction studies revealed that the structure is face centered monoclinic in the absence of benaldehyde and monoclinic in the presence of tartaric acid. There is no significant change in the percentage composition of the alloy by the addition of additives. The obtained XRD patterns represented a face centered monoclinic in the absence of additives and monoclinic in the presence of benzaldehyde. Inclusion of additives by adsorption on the deposit enhances corrosion protection in the stimulated aggressive environment (0.05 M H_2SO_4 medium). Tafel polarization studies exhibited a decrease in the corrosion rate when benzaldehyde (0.75g/L) is added to the electrolyte. The higher R_{ct} value of the coating deposit in the presence of 0.75g/L benzaldehyde implies enhanced corrosion resistance compared to that of deposit in the presence of tartaric acid. Electrochemical results obtained are relatively in agreement with weight loss technique. Good corrosion resistance of Zn-Ni alloy electrodeposition with benzaldehyde additive revealed that it can be alternatively used for cadmium coating.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. H.P. Sachin, G. Achary, Y.A. Naik and T.V. Venkatesha, *Bull. Mater. Sci.*, **30**, 57 (2007); https://doi.org/10.1007/s12034-007-0010-0.
2. U.P. Kumar and C.J. Kennady, *Int. J. Miner. Metall. Mater.*, **22**, 1060 (2015); https://doi.org/10.1007/s12613-015-1168-x.
3. J. Liu, W. Yu, J. Zhang, S. Hu, L. You and G. Qiao, *Appl. Surf. Sci.*, **256**, 4729 (2010); https://doi.org/10.1016/j.apsusc.2010.02.082.
4. http://coursenotes.mcmaster.ca/4L04/Thin_Films/Electrodeposition_of_Metal.pdf.
5. L.J. Durney, Electroplating Engineering Handbook, Van Nostrand Reinhold Company, edn 4 (1984).
6. B.N. Chapman and J.C. Anderson, Science and Technology of Surface Coating, Academic Press Inc.: London, p. 69 (1974).
7. S.H. Mosavat, M.E. Bahrololoom and M.H. Shariat, *Appl. Surf. Sci.*, **257**, 8311 (2011); https://doi.org/10.1016/j.apsusc.2011.03.017.
8. F. Xiao, X. Shen, F. Ren and A.A. Volinsky, *Int. J. Miner. Metall. Mater.*, **20**, 472 (2013); https://doi.org/10.1007/s12613-013-0753-0.
9. C.A. Loto, Corrosion Prevention and Control, Influence of Organic Additives on the Surface Characteristics of Zinc Electrodeposition on Mild Steel in Acid-Chloride Solution: pH, Bath-Composition and Time. eprints (1992).
10. M.P.Q. Argañaraz, S.B. Ribotta, M.E. Folquer, E. Zelaya, C. Llorente, J.M. Ramallo-López, G. Benítez, A. Rubert, L.M. Gassa, M.E. Vela and R.C. Salvarezza, *Electrochim. Acta*, **72**, 87 (2012); https://doi.org/10.1016/j.electacta.2012.03.163.
11. V. Ravindran, Ph.D. Thesis, Alagappa University, Karaikudi, India (1994).
12. C.C. Koch, *J. Mater. Sci.*, **42**, 1403 (2007); https://doi.org/10.1007/s10853-006-0609-3.
13. A. Chianpairot, G. Lothongkum, C.A. Schuh and Y. Boonyongmaneerat, *Corros. Sci.*, **53**, 1066 (2011); https://doi.org/10.1016/j.corsci.2010.12.001.
14. M. Furko, Y. Jiang, T. Wilkins and C. Balázsi, *Ceram. Int.*, **42**, 4924 (2016); https://doi.org/10.1016/j.ceramint.2015.12.006.
15. U.P. Kumar, C.J. Kennady and Q. Zhou, *Surf. Coat. Technol.*, **283**, 148 (2015); https://doi.org/10.1016/j.surfcoat.2015.10.056.
16. W. Ye, Y. Li and F. Wang, *Electrochim. Acta*, **51**, 4426 (2006); https://doi.org/10.1016/j.electacta.2005.12.034.
17. K.R. Sriraman, S.G. Sundara Raman and S.K. Seshadri, *Mater. Sci. Eng. A*, **460–461**, 39 (2007); https://doi.org/10.1016/j.msea.2007.02.055.
18. G.Y. Wei, H.L. Ge, X. Zhu, Q. Wu, J.Y. Yu and B.Y. Wang, *Appl. Surf. Sci.*, **253**, 7461 (2007); https://doi.org/10.1016/j.apsusc.2007.03.045.