Optimizing Electroless Plating of Ni–Mo–P Coatings Toward Functional Ceramics

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Abstract

Ni–Mo–P coatings are obtained at the surface of ceramic substrate by electroless deposition using palladium as a surface catalyst. The influence of catalyst activation conditions on coatings' properties was assessed by structural, morphological, electrical, mechanical measurements and adhesion strength by using X-ray diffraction, field emission scanning electron microscopy, atomic force microscopy, Hall effect and nanoindentation techniques, respectively. The results indicated the formation of dense, continuous and uniform coatings consisting mainly of Ni. The coatings obtained at 300 °C for 12 h exhibited the best electrical properties, namely resistivity of 9.32 $\mu\Omega$ cm, smaller roughness (R_a 0.090 μ m) and average mechanical properties. The adhesion tests showed a firm adherence of the Ni–Mo–P coatings to the ceramic surface. The results of this study could offer an approach for obtaining conducting ceramic substrates in order to be employed in photovoltaic applications. The performance of demonstrative heterojunction solar cell obtained with such metallized ceramic is indicative of the high potential of the Ni–Mo–P electroless coatings for functional ceramics.

Keywords Electroless plating · Ni–Mo–P · Ceramic · Solar cell

1 Introduction

Ceramic materials have been extensively used for building applications thanks to their excellent chemical performance and environmental resistance, as well as relevant mechanical, thermal and hardness properties. However, new opportunities appear for functional ceramic substrates which could extend their scope in other areas such as electronic devices [1], photovoltaic [2] and photoelectrochemical or photocatalytic fields [3, 4]. For this end, ceramic substrates require electrical functionality such as surface conductivity [5] that

may be achieved by depositing a metallic coating by different methods including chemical and physical vapor deposition or electroless methods [6, 7].

Electroless deposition (ED) [8] is a low-cost, easily applied and scaled process without restrictions in regard to the nature and shape of the substrate, thus allowing the deposition of homogeneous alloy coatings with uniform thickness on a non-conductive surface [5, 9–14]. As a function of the given material, the ED could improve some of their surface properties such as conductivity [15], durability, microhardness [16], service time and substrate lubricity [17]. In addition to such mechanical and physical properties, the ED deposition is also used to tailor the optical properties and can generate catalytic surfaces [18]. ED is an autocatalytic hydro process [14, 19] for preparing metallic coatings without electrical power [5, 20]. Depending on the composition bath of ED, in some cases, this process can be considered as an environmentally friendly technology for obtaining a metallic layer due to the absence of dangerous metal sources or reducing, complexing and gloss agents based on cyanides, Pb^{2+} , EDTA, Cd^{2+} and formaldehyde, respectively [21]. It is carried out by two steps: surface activation and electroless metallization. In some cases, a final thermal treatment is required in order to enhance final results. According to

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Kobets and Vorobyova [10], the surface activation process can be carried out by plunging the non-conductive substrate into SnCl_2 solution, followed by sensitization process with an acid solution of PdCl_2 . However, contamination of the palladium layer with residual Sn particles may occur, resulting in impaired stability of the layer at high temperatures. In order to avoid these issues, a selective catalysis could be achieved by using a Pd organic layer and subjecting it to thermal activation/reduction in air or in an inert atmosphere (hydrogen) [22, 23].

The ED process of Ni coatings has been studied in depth lately due to their mechanical properties or resistance to corrosion, wear and friction [24–26] and their electrocatalytic activity [27]. Overall, ED of Ni could lead to Ni–X–P or Ni–X–B coatings, where X could be an alloying metal or a composite particle (such as W, Cu, Zn, Co, CNTs), P is phosphorus and B is boron [14, 25]. Phosphorus is an alloying element which modifies the crystal lattice and allows high operating temperatures [24, 28]. Moreover, the hypophosphite source of P is known for the reducing property [29]. For improving the mechanical properties such as hardness and corrosion resistance, Mo can be added during electroless plating to form a ternary alloy [30] given its anti-pitting properties [31, 32]. Besides, Mo can enhance stability and solubility in the Ni phases and enhance the thermal stability [24, 33, 34]. Therefore, Ni–Mo–P coating has excellent corrosion and wear resistances as well as high hardness [34].

One of the main drawbacks of ED is the poor adhesion between the metallic layer and ceramic surface, which basically depends on the mechanical bond generated by metal–ceramic anchoring effects [35], as well as on the properties of the base material (e.g., roughness) and the conditions of the process (e.g., pH) [1, 22, 36]. In order to improve the coating adherence to the ceramic substrate, surface treatments including chemical and/or mechanical process [10] should be carried out prior to the electroless process in order to allow the generation of impurity-free surfaces with a homogeneous roughness [1]. For example, the thermal projection of a micro-sized Ni layer onto the ceramic substrate was employed prior to applying the catalyst ink so as to enhance the adherence of a Ni–Mo coating [37].

Despite the achievements obtained in the field, a proper balance between adhesion and surface properties of the coating is advised in order to confer the obtained coated ceramics with functionality. Moreover, it is considered that a study on cost- and time-efficient electroless deposition of conductive films onto ceramics is highly required. Therefore, this study is focused on improving the knowledge on the influence of Pd catalyst ink activation conditions on the surface properties of electroless Ni–Mo–P coatings. The novelty of the work resides in the use of ceramic substrate, absence of any prior pre-treatment and the improved activation conditions for the catalyst ink toward conductive coatings. For the

potential applicability of such metallized ceramic substrate, a heterojunction solar cell is fabricated and tested. The results presented in this work are beneficial for the fabrication of functional ceramics and conductive coatings required in photovoltaic applications [38].

2 Materials and Methods

2.1 Materials

Palladium acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Pd}$), nickel sulfate (NiSO_4), sodium molybdenum (Na_2MoO_4), sodium hypophosphite (NaH_2PO_2), gluconic acid 50% ($\text{C}_6\text{H}_{12}\text{O}_7$), sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$), ammonium hydroxide (NH_4OH) and 1-propanol ($\text{C}_3\text{H}_8\text{O}$) were purchased from Alfa Aesar. Butter Polyvinyl Butyral Resin B-98 (Butvar) was purchased from Acros Organics. Ceramic substrates were prepared from a commercial porcelain stoneware atomized powder, pressed under standard conditions and heated at 1.100°C with a loss of incineration of 11.86%. The chemical composition (wt%) of commercial atomized powder is 59.85% SiO_2 , 15.99% Al_2O_3 , 0.48% Fe_2O_3 , 4.87% CaO , 3.59 of MgO , 1.45% Na_2O , 1.30% K_2O and 0.61% Ti_2O . All measurements were repeated for five times.

2.2 Pd Catalyst Ink Activation

To activate the ceramic surface, a Pd catalyst ink was prepared. The ink formulation was prepared as follows: Solution (A) containing 1 g of Butvar in 50 mL of 1-propanol was continuously stirred for 2 h. Solution (B) consisting of 0.19 g of palladium acetate in 0.5 mL of ammonium hydroxide was added to the solution (A) to form the Pd catalyst ink [37, 39]. Prior to use, the Pd catalyst ink was stirred for 24 h at 250 rpm. The ceramic substrates were airbrushed with the Pd catalyst ink for three times and dried each time at 60°C . The catalyzed samples were activated at 300 and 400°C for 12 and 24 h in an oven with ambient atmosphere.

2.3 Electroless Deposition of Ni–Mo–P Coating

Upon the activation process with Pd, the ceramic substrates were immersed in the Ni–Mo–P plating bath. The Ni–M–P deposition bath consisted of 7.0 g L^{-1} NiSO_4 and 3.9 g L^{-1} Na_2MoO_4 as metallic precursor, 10 g L^{-1} NaH_2PO_2 as reducing agent, 10.0 g L^{-1} $\text{C}_6\text{H}_{12}\text{O}_7$ and 15 g L^{-1} $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ as stabilizing agents and NH_4OH as complexing agent and pH adjuster [2, 37]. The electroless deposition was performed at pH 10, 80°C , for 30 min with constant stirring at 300 rpm. Finally, the substrates were rinsed with water to finish the reaction and air-dried. The obtained Ni–Mo–P coatings were denominated as Ni–Mo–P₍₃₀₀₋₁₂₎, Ni–Mo–P₍₄₀₀₋₁₂₎,

Ni–Mo–P₍₄₀₀₋₁₂₎ and Ni–Mo–P₍₄₀₀₋₂₄₎ coatings, as a function of activation temperature and time. The Ni–Mo–P-coated ceramic substrates were further annealed at 400 °C for 3 h [12] in order to study the modifications of the coating microstructure [28, 36].

2.4 Ceramic-Supported Solar Cell Fabrication

Once optimized, the parameters for electroless deposition of Ni–Mo–P onto ceramic substrate were employed in order to fabricate a demonstrative ZnO/Cu₂O heterojunction solar cell. The fabrication procedure presented by Rosas et al. [40] involves the two-step electrochemical deposition of the heterojunction layers. For such aim, the Ni–Mo–P metallized ceramic (5 cm × 1.3 cm) serves as cathode in an electrochemical cell. The Pt foil served as counter electrode while the reference electrode consisted of Ag/AgCl in saturated KCl. Then, ZnO layer was electrodeposited at –0.8 V at 80 °C for 1 h on 4 cm × 1.3 cm of metallized ceramic and the Cu₂O layer was successively electrodeposited at –0.6 V at 40 °C for 5 h onto 2.5 cm × 1.3 cm of ZnO layer, upon rinsing and air-drying. The top coating of solar cell consisted of a conductive carbon cement (Leit-C). The illumination direction is perpendicular to the cell, from the carbon side. The un-coated part of ZnO layer serves as window for the photons.

2.5 Characterization

Structural parameters were determined by X-ray diffraction (XRD, Rigaku Ultima IV diffractometer) using Cu K α radiation (Cu K α = 1.54 Å). The roughness of the surface was measured by using a tapping/contact-mode atomic force microscope (AFM, Bruker Multimode 8). The morphology, thickness and elemental analysis were assessed by field emission scanning electron microscopy with focused ion beam (FIB) (FE-SEM, Auriga Compact, Zeiss) and energy-dispersive X-ray spectrometer (EDS). The adhesion strength between the coatings and the ceramic was evaluated using an automatic adhesion tester (PosiTest AT-100, DeFelsko, USA). The test procedure consisted of preparing a specimen made of metallic disk (dolly) which was glued on the Ni–Mo–P coatings by thermosetting adhesive (Araldite series 2000). The adhesive was cured at an ambient temperature for 48 h to obtain stronger adhesion between the dolly and coating. The adhesion test was carried out by pulling the dolly from the sample coating in the direction normal to the coating surface until the adherence fails and the coating is peeled-off [41]. The electrical resistivity of Ni–Mo–P coatings on the ceramic substrate was measured using the Hall effect method and considered the corresponding thickness of Ni–Mo–P coating. Finally, the hardness and elastic modulus of the samples

were measured by using a G200 nanoindenter (Agilent Technologies, USA) and a maximum indentation depth of 2000 nm. The stiffness was measured by CSM (continuous stiffness), where the harmonic oscillation amplitude and oscillation frequency were 2 nm and 45 Hz, respectively. The photoelectrical properties of the ceramic-supported heterojunction solar cell were measured with a Sun 2000 Solar Simulator (ABET Technologies) under 800 W m^{–2} irradiation through the ZnO layer in a similar design as reported elsewhere [42–44].

3 Results and Discussion

Firstly, the structure of the ceramic substrate was observed by XRD as shown in Fig. 1a. The peaks identified in the spectrum are attributed to SiO₂ (PDF Card No.: 00-033-1161), Al₂O₃ (PDF Card No.: 00-021-0010), CaO (PDF Card No.: 00-028-0775), Mg(O₂)₂ (PDF Card No.: 00-027-0759), Na₂O (PDF Card No.: 00-023-0528), K₂O (PDF Card No.: 00-039-0697) and K₂O₂ (Card No.: 00-032-0827), and they are in agreement with the composition of atomized powder.

The crystal structure of the Ni–Mo–P coatings obtained by ED prior and upon annealing treatment was determined by XRD analysis as shown in Fig. 1b. It is evident that the structure of the Ni–Mo–P coating is crystalline in all samples. Typical peaks including Ni (111), corresponding to face-centered cubic phase of Ni [45], and Ni (200) appear at ~44° and ~52° [46], respectively. No phosphorous or molybdenum peaks appear in the spectra which is due to the presence of such elements as solute in nickel. Compounds such as Ni₃P are absent as well. Although the peaks of the substrate are still intense, it can be observed that no significant differences were observed for the samples obtained at a Pd catalyst activation temperature of 300 °C and varying durations. On the other hand, by increasing the Pd catalyst activation temperature to 400 °C, one can observe the intensity of the preferential growth plane of the Ni–Mo–P coating, namely Ni(111), diminishes, while Ni(200) peak intensity remains unmodified. These findings suggest a detrimental effect of increasing Pd activation temperature on the crystalline structure of the coatings, and it can be attributed to variation in nucleation sites on the Pd ink coating during the growth of the Ni–Mo–P coating [39]. Annealing appears to improve the crystalline structure of the Ni–Mo–P coatings as indicated by the slight increase in the intensity of Ni(111) peak depicted in Fig. 1c, besides the smaller related FWHM which indicates larger crystallite size.

Crystallite size values were obtained by considering the Ni(111) predominant reflection [25] and the Scherrer's equation [47]:

Fig. 1 X-ray diffraction patterns of **a** ceramic substrate, Ni–Mo–P coatings **b** before and **c** after annealing

$$D = \frac{0.9}{\beta \cos \theta}, \quad (1)$$

where D is the average crystallite size, λ is the X-ray wavelength (1.54 Å), β is FWHM (full width at half maxima, in rad) and θ is the diffraction angle (in degrees). While the calculated crystallite sizes are similar (e.g., 14.53 and 20.93 nm for Ni–Mo–P₍₃₀₀₋₁₂₎ and Ni–Mo–P₍₃₀₀₋₂₄₎, respectively), it was observed that the annealing treatment induces

Fig. 2 Thickness and roughness (R_a) of Ni–Mo–P coatings before and after heat treatment (HT)

no significant variation in the crystallite size for the coatings obtained at a catalyst activation temperature of 300 °C which indicates a good crystalline structure stability. On the other hand, when the catalyst is activated at 400 °C, an increase in the crystallite size up to 27.75 nm is observed upon annealing of the corresponding coatings.

Thickness of Ni–Mo–P coatings was measured by FE-SEM after FIB sample cross sectioning, and roughness measurements for ceramic substrate and Ni–Mo–P coatings before and after annealing treatment were taken by statistical AFM analysis on all samples for R_a (arithmetic mean) as shown in Fig. 2. Thickness of Ni–Mo–P coatings appears similar irrespective of the catalyst conditions, as it varies from 480 to 522 nm. In this study, the initial R_a of ceramic substrate is 268.0 ± 69.5 nm. The R_a of the Ni–Mo–P coatings was observed to increase with time for the coatings obtained at activation temperature of 300 °C and to decrease in case of catalyst activation at 400 °C. Annealing treatment resulted in lower R_a values for all samples, with a stronger effect on the coatings obtained by catalyst activation at 400 °C possibly due to an Ostwald ripening effect at higher temperature [48].

The FE-SEM images depicted in Fig. 3 show the evolution of film section and morphology of Ni–Mo–P coatings onto ceramic substrates with Pd catalyst activation and annealing treatment (400 °C for 3 h). The insets in Fig. 3a–d show the catalyst morphology as a function of activation conditions. It can be clearly observed that the higher temperature induces the formation of larger grains which is due to faster growth kinetics, while the longer duration results in more homogeneous films with higher density of grains. The as-deposited Ni–Mo–P coatings (Fig. 3e–h) exhibit

Fig. 3 Film section (Pd catalyst morphology in inset) (a–d), film morphology before annealing (higher magnification in inset) (e–h), after annealing (i–l) as function of synthesis conditions

the typical morphology of cauliflower nodules [24] and cover uniformly and continuously all the ceramic surface. The micrographs show a nodular morphology with cracks which disappear upon annealing treatment due to an Ostwald ripening effect [24, 49]. Depending on Pd catalyst activation, various morphology changes are observed: The coatings obtained at activation temperature of 300 °C exhibit a smooth surface independently on the activation time, while catalyst activation at 400 °C induces some cracks at the surface possibly due to increased growth kinetics. Nevertheless, the surfaces get smoother upon annealing, thus resulting in lower surface roughness. The Ni–Mo–P₍₃₀₀₋₁₂₎ coating appears to be the smoothest which is attributed to homogeneous growth rate of the nuclei formed at 300 °C.

EDS analysis was carried out in order to determine the chemical element content (wt%) of Ni–Mo–P coatings onto ceramic substrates. Figure 4 shows the EDS spectra of Ni–Mo–P as a function of catalyst activation temperature and time and in the line spectrum of EDS at the cross section

of the coating. As one can observe, all the spectra are similar and show nickel (Ni), phosphorous (P) and molybdenum (Mo) elements corresponding to XRD analysis. The element composition of the coatings is ~84.8% Ni [34], while P content is ~1.9%, which corresponds to low P (1–5%) coating [30, 46], and ~13.3% Mo. According to Guo et al. [46], there is a direct relation between P content and crystallinity of Ni–P coating due to the low solubility of P in Ni. That is, a low P content usually results in a crystalline coating, while a high P content induces the formation of an amorphous coating. Figure 4d shows a representative variation of Ni, Mo and P contents along the cross section of the Ni–Mo–P coating onto ceramic substrate. The coatings largely consisted of Ni (85%) in comparison with Mo and P content corresponding to a depth of 1.6 μm, after which the Ni, Mo and P contents decrease significantly as the scan approaches the ceramic substrate.

The adhesion strength of the electroless coatings onto ceramic as effect of different Pd catalyst activation was

Fig. 4 EDX spectra for the Ni–Mo–P coatings prepared at **a** 300 °C for 12 h, **b** 400 °C for 12 h, **c** 400 °C for 24 h, **d** line spectrum of EDS analysis in the cross section of the coating

Fig. 5 Adhesion strength of Ni–Mo–P coating. Inset shows digital images of adhesion measurement: sample upon annealing (**a**), upon adhesion test (**b**), after glue removal (segmented line) (**c**)

tested with PosiTest AT-A. Representative images of coated ceramics after adhesion test are depicted in Fig. 5. Pd layer was not affected during adhesion tests as indicated by the

dark mark at the surface of ceramic substrate. It should be noted that all coatings exhibited improved adhesion strength with respect to the reported literature, and Shi et al. [50] have found that adhesion strength of Ni–Mo–P coatings onto birch veneers substrate ranges between 1.7 and 2.3 MPa. Interestingly, similar adhesion strength of the Ni–Mo–P coatings was obtained for catalyst activation at 400 °C irrespective of the catalyst activation duration. On the other hand, the adhesion improved by increasing the activation temperature from 300 to 400 °C, in agreement with higher roughness observed previously. The improved adhesion of the coatings obtained upon catalyst activation at higher temperature is attributed to the anchorage effect between the coating/catalyst layer/substrate interfaces. The annealing treatment efficiently improved their adhesion.

The resistivity measurements with catalyst activation conditions such as duration and temperature are further depicted in Fig. 6. Generally, the resistivity of electroless coatings was indicated to depend on parameters including bath composition, thickness and structure of the coating and deposition time [50, 51]. While the film resistivity is thickness dependent [52], in this study, the catalyst activation conditions are shown to induce only a small variation

Fig. 6 Evolution of hardness, elastic modulus and volume resistivity of Ni–Mo–P coatings as a function of catalyst activation conditions

in the thickness of electroless coating as shown in Fig. 3 but the changes in resistivity are significant. It is observed that low catalyst activation temperature and time resulted in the best electrical properties, namely $10.6 \pm 2.2 \mu\Omega \text{ cm}$. By increasing Pd catalyst activation temperature for 12 h, the resistivity values of electroless Ni–Mo–P coatings increase with about 102% and by increasing activation duration from 12 to 24 h the resistivity increased with almost 42%, reaching $76.3 \pm 17.4 \mu\Omega \text{ cm}$ at 400 °C for 24 h, which could be explained by increased roughness or cracks in the coatings at higher catalyst activation temperature or longer time. Such behavior could be explained by the dependence of Ni–Mo–P growth on the anchored Pd seeds. Thus, at lower temperature and time, the Pd seeds are smaller and in a higher density [39]; thus, in these conditions, the Pd catalyst seeds could foster the growth of smaller Ni–Mo–P grains with an even distribution. The higher the number of activation sites with smaller activity, the smaller the Ni–Mo–P crystallite size, which results in a more conductive and even Ni–Mo–P metallic layer. On the other side at higher temperature, the catalyst seeds are larger and foster the growth of larger Ni–Mo–P grains, which further results in the appearance of cracks, and therefore, the resistivity increases. Additionally, the coating obtained at 400 °C for 24 h shows (Fig. 4) grains onto its surface which reflects a change in the growth process due to the nuclei formed on the catalyst layer. Annealing of the ED coatings further increases their resistivity which could be due to the loss in density of carriers by reaction with oxygen or due to grain boundary effects [53].

The increase in electric resistivity of the Ni–Mo–P coatings is undesirable for many applications including photovoltaic ones. As given in Table 1 presenting the resistivity

Table 1 Resistivity of Ni–P and Ni–Mo–P-based coatings on different substrates

Substrate	Coating	Resistivity ($\Omega \text{ cm}$)	References
PEEK/MWCNT composites	Ni–P	100	[60]
PET	Ni–P	0.09	[51]
Silicon	Ni–P	10^{-3} and 10^{-5}	[36]
Glass fabric	Ni–P	6.25×10^{-3}	[61]
Glass fibers	Ni–P	$(7.36 \pm 0.37) \times 10^{-3}$	[62]
PET	Ni–P	1.9×10^{-4}	[9]
B–Si(100) wafers	Ni–Mo–P	5.72×10^{-5}	[63]
Birch veneers ^a	Ni–Mo–P	208	[50]
Ceramic	Ni–Mo–P	9.32×10^{-6}	This work

^aSurface resistivity ($\text{m}\Omega \text{ cm}^{-2}$)

values for the electroless Ni–P and Ni–Mo–P coatings deposited on varying substrates, the values obtained for the Ni–Mo–P coatings in this work at low catalyst activation temperature and time are markedly improved with respect to the literature, highlighting the importance of Pd catalyst activation conditions for the fabrication of conductive electroless coatings.

The requirements for a functional coating include a balance of adhesion, mechanical and electrical properties of the obtained electroless Ni–Mo–P coatings. The values of hardness and elastic modulus were measured by nanoindentation and calculated by Oliver–Pharr method [54], using a Poisson coefficient of 0.18. It is evident from Fig. 6 that the mechanical properties of the coatings are dependent on the Pd catalyst activation conditions. Thus, the hardness and elastic modulus are observed to decrease with an increase in catalyst activation temperature from 300 to 400 °C. On the other hand, the hardness and elastic modulus increase with catalyst activation time, reaching about 6 GPa and 90 GPa, respectively, in the case of Ni–Mo–P coating obtained when the catalyst was activated at 300 °C for 12 h. While these results are similar to those shown for a Ni–P coating deposited on carbon steel [55], they are still lower than the ones reported by Song et al. for a Ni–P coating deposited on aluminum (7.01 GPa and 153.5 GPa, respectively) [30], which could be explained by the absence of Ni_3P precipitates [34, 56], in agreement with Fig. 1b. In order to explain the effect of catalyst activation on the mechanical properties of electroless Ni–Mo–P coatings, the residual stresses during coating process as a consequence of thermal mismatch, or during mechanical and thermal processes [31], must be taken into account as they can change the interatomic distances.

For the sake of demonstrative applicability of the electroless Ni–Mo–P coatings and ceramic support, a heterojunction solar cell with the structure defined in Fig. 7 was fabricated. The p and n layers consisting of ZnO and Cu_2O

Fig. 7 Typical I–V curve of the Cu₂O/ZnO/ceramic heterojunction under illumination. The lower inset shows the structure of the solar cell

films were successively electrodeposited on the metallized ceramic. While the theoretical power conversion efficiency of ZnO/Cu₂O is around 18% [57], an electrodeposited heterojunction cell could only achieve 1.43% with a short-circuit current density (J_{sc}) of 4.47 mA cm⁻² and open-circuit voltage (V_{oc}) of 0.535 (V) by electrodeposition process [58] until now. In this study, the photoelectrical measurement indicated a J_{sc} of 0.098 mA cm⁻² and V_{oc} of 104.56 mV. While still low, the results are in line with the relevant literature on similar electrodeposited heterojunction solar cell [59]. The photovoltaic result is attributed to the interface properties induced by the ZnO morphology and demonstrates the suitability of electroless Ni–Mo–P coating for functional ceramics.

4 Conclusions

Electroless Ni–Mo–P coatings are obtained at the surface of porcelain stoneware surfaces in varying catalyst activation conditions, namely temperature and duration. By comparing the properties of the coatings obtained in varying catalyst activation conditions, it was observed that by using 300 °C for 12 h, the coating shows a stable crystalline structure and smoother typical cauliflower modular morphology. As indicated by XRD measurements, a detrimental effect of increasing Pd activation temperature on the crystalline structure of the coatings is observed and it can be attributed to varying nucleation processes on Pd ink coating. The obtained coatings exhibit improved adhesion strength, while their hardness and elastic modulus are observed to decrease with increasing the catalyst activation temperature from 300

to 400 °C due to residual stress during process. The lowest resistivity ($9.32 \times 10^{-6} \Omega \text{ cm}$) is attributed to the smaller and denser catalyst seed formation at lower catalyst activation temperature and time. The photoelectrical results of the fabricated heterojunction solar cell obtained with electroless Ni–Mo–P-coated ceramic demonstrate the applicability of optimized electroless coating of Ni–Mo–P layers to fabricate functional ceramics.

The results show that the catalyst activation conditions such as temperature and duration are of paramount importance for the fabrication of conductive electroless coatings which could be applied for varying applications such as photovoltaic devices upon considering a proper balance between adhesion and surface properties.

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References

- [1] X. Zheng, J. Tan, Q. Zhang, M. Wang, L. Meng, *Surf. Coat. Technol.* **311**, 151 (2017)
- [2] M.D. Reyes-Tolosa, M. Ajami, J. Orozco-Messana, V. Donderis, M. Pascual, M.A. Hernández-Fenollosa, *Cerámica y Vidr.* **49**, 351 (2010)
- [3] A. Currao, *Chim. Int. J. Chem.* **61**, 815 (2007)
- [4] D. Bae, B. Seger, O. Hansen, P.C.K. Vesborg, I. Chorkendorff, *ChemElectroChem* **6**, 106 (2019)
- [5] A. Heidarzadeh, R.T. Mousavian, R.A. Khosroshahi, Y.A. Afkham, H. Pouraliakbar, *Rare Met.* **36**, 209 (2017)
- [6] A. Atli, S. Simon, F.J. Cadete Santos Aires, L. Cardenas, E. Ehret, P. Lourdin, *J. Appl. Polym. Sci.* **134**, 17 (2017)
- [7] R.H. Guo, S.X. Jiang, Y.D. Zheng, J.W. Lan, *J. Appl. Polym. Sci.* **127**, 4186 (2012)
- [8] V. Vitry, F. Delaunois, C. Dumortier, *Surf. Coat. Technol.* **202**, 3316 (2008)
- [9] H. Wu, A. Susanto, K. Lian, *Appl. Surf. Sci.* **394**, 63 (2017)
- [10] A.V. Kobets, T.N. Vorobyova, *Thin Solid Films* **616**, 793 (2016)
- [11] J.D. Lin, C.L. Kuo, *Surf. Coat. Technol.* **209**, 80 (2012)
- [12] J. Cao, H. Yi, Z. Zang, *Adv. Intell. Syst. Res.* **130**, 1240 (2016)
- [13] A.A. Zuleta, M. Ojewumi, Y.D. Yeboah, E.E. Kalu, O. Elendu, M. Ojewumi, Y.D. Yeboah, E.E. Kalu, *Int. J. Electrochem. Sci.* **25**, 778 (2016)
- [14] J. Jiang, H. Chen, Y. Wang, L. Zhu, Y. Sun, H. Lin, S. Han, Y. Luo, W. Qian, *Surf. Eng.* **35**, 873 (2019)
- [15] F.T. Zhang, L. Xu, J.H. Chen, B. Zhao, X.Z. Fu, R. Sun, Q. Chen, C.P. Wong, *A.C.S. Appl. Mater. Interfaces* **10**, 2075 (2018)
- [16] M. Alishahi, S.M. Monirvaghefi, A. Saatchi, S.M. Hosseini, *Appl. Surf. Sci.* **258**, 2439 (2012)
- [17] R. Jiang, X. Zhou, Z. Liu, *Mater. Sci. Eng. A* **679**, 323 (2017)
- [18] C.L. Lee, C.C. Wan, Y.Y. Wang, *J. Electrochem. Soc.* **150**, C125 (2003)
- [19] X. Xu, Z.D. Cui, S.L. Zhu, Y.Q. Liang, X.J. Yang, *Surf. Coat. Technol.* **240**, 425 (2014)
- [20] I.G. Serin, A. Göksenli, B. Yüksel, R.A. Yildiz, *J. Mater. Eng. Perform.* **24**, 3032 (2015)

- [21] B. Zhang, *Amorphous and Nano Alloys Electroless Depositions. Technology, Composition, Structure and Theory* (Elsevier, Amsterdam, 2016), pp. 383–409
- [22] F. Roa, J.D. Way, *Ind. Eng. Chem. Res.* **42**, 5827 (2003)
- [23] J.D. Way, R.L. McCormick, F. Roa, S.S.N. Paglieri, *Chem. Eng. J.* **93**, 11 (2003)
- [24] A. Mukhopadhyay, T.K. Barman, *Surf. Rev. Lett.* **25**, 1 (2018)
- [25] A. Mukhopadhyay, T.K. Barman, P. Sahoo, *Mater. Res. Express* **5**, 26526 (2018)
- [26] V. Vitry, E. Francq, L. Bonin, *Surf. Eng.* **35**, 159 (2019)
- [27] G. Krishnamurthy, M.S. Shivakumar, *J. Appl. Electrochem.* **47**, 519 (2017)
- [28] I. Apachitei, F.D. Tichelaar, J. Duszczek, L. Katgerman, *Surf. Coat. Technol.* **149**, 263 (2002)
- [29] B. Zhang, *Amorphous and Nano Alloys Electroless Depositions. Technology, Composition, Structure and Theory* (Elsevier, Amsterdam, 2016), pp. 51–106
- [30] G.S. Song, S. Sun, Z.C. Wang, C.Z. Luo, C.X. Pan, *Acta Metall. Sin. (Engl. Lett.)* **30**, 1008 (2017)
- [31] H. Liu, D.S. Qian, *Trans. Nonferrous Met. Soc. China (Engl. Ed.)* **28**, 2499 (2018)
- [32] H. Liu, Z. Liu, *Surf. Coat. Technol.* **330**, 270 (2017)
- [33] B. Zhang, *Amorphous and Nano Alloys Electroless Depositions. Technology, Composition, Structure and Theory* (Elsevier, Amsterdam, 2016), pp. 323–381
- [34] H. Liu, P. Wang, Z. Liu, G. Harrison, G.E. Thompson, *Trans. IMF* **94**, 76 (2016)
- [35] H. Honma, T. Komatsuzawa, *Adv. Mater. Manuf. Process.* **3**, 291 (1988)
- [36] B.H. Liu, F.Y. Liao, J.H. Chen, *Thin Solid Films* **537**, 263 (2013)
- [37] M.D. Reyes-Tolosa, E.E. Kalu, J. Orozco-Messana, A. Erb, P.N. Kalu, M.A. Hernández-Fenollosa, H.J. Bolink, *ECS Trans.* **25**, 81 (2010)
- [38] J.K. Pancrecius, S.B. Ulaeto, R. Ramya, T.P.D. Rajan, B.C. Pai, *Int. Mater. Rev.* **63**, 488 (2018)
- [39] A.S. Kuruganti, K.S. Chen, E.E. Kalu, *Electrochem. Solid-State Lett.* **2**, 27 (1999)
- [40] N.M. Rosas-Laverde, A. Pruna, J. Cembrero, J. Orozco-Messana, F.J. Manjón, *Boletín La Soc. Española Cerámica y Vidr.* (2019). <https://doi.org/10.1016/j.bsecv.2019.06.002>
- [41] P. Carpio, E. Rayón, M.D. Salvador, L. Lusvarghi, E. Sánchez, *J. Therm. Spray Technol.* **25**, 778 (2016)
- [42] W. Septina, S. Ikeda, M.A. Khan, T. Hirai, T. Harada, M. Matsumura, L.M. Peter, *Electrochim. Acta* **56**, 4882 (2011)
- [43] M. Yang, L. Zhu, Y. Li, L. Cao, Y. Guo, *J. Alloys Compd.* **578**, 143 (2013)
- [44] M. Plawecki, E. Rówiński, L. Mieszczak, *Acta Phys. Pol. A* **130**, 1144 (2016)
- [45] J.N. Balaraju, N. Raman, N.T. Manikandanath, *Trans. IMF* **92**, 169 (2014)
- [46] Z. Guo, K.G.G. Keong, W. Sha, *J. Alloys Compd.* **358**, 112 (2003)
- [47] H. Lahmar, F. Setifi, A. Azizi, G. Schmerber, A. Dinia, *J. Alloys Compd.* **718**, 36 (2017)
- [48] A.G. González, P.J. Sebastian, L.M. Cacho, J. Campos, A. Baron, E.B. Arco, *Int. J. Electrochem. Sci.* **13**, 3958 (2018)
- [49] H. Liu, R.X. Guo, F. Viejo, Z. Liu, *Surf. Coat. Technol.* **206**, 2380 (2012)
- [50] C. Shi, L. Wang, L. Wang, *RSC Adv.* **5**, 104750 (2015)
- [51] Z. Sun, J. Huang, L. Wang, X. Zhang, M. Li, B. Tang, *J. Mater. Sci. Mater. Electron.* **26**, 10132 (2015)
- [52] A. Goktas, F. Aslan, E. Yasar, I.H. Mutlu, *J. Mater. Sci. Mater. Electron.* **23**, 1361 (2012)
- [53] A. Goktas, F. Aslan, A. Tumbul, *J. Sol-Gel. Sci. Technol.* **75**, 45 (2015)
- [54] Q. Yu, T. Zhou, Y. Jiang, X. Yan, Z. An, X. Wang, D. Zhang, T. Ono, *Appl. Surf. Sci.* **435**, 617 (2018)
- [55] A. Mejias, D. Chicot, A. Pertuz, A. Iost, A. Montagne, P. Cadenas, *Surf. Coat. Technol.* **334**, 410 (2018)
- [56] M. Sribalaji, O.S. Asiq Rahman, T. Laha, A.K. Keshri, *Mater. Chem. Phys.* **177**, 220 (2016)
- [57] A.E. Gunnaes, S. Gorantla, O.M. Lovvik, J. Gan, P.A. Carvalho, B.G. Svensson, E.V. Monakhov, K. Bergum, I.T. Jensen, S. Dip-las, *J. Phys. Chem. C* **120**, 23552 (2016)
- [58] K. Fujimoto, T. Oku, T. Akiyama, *Appl. Phys. Express* **6**, 086503 (2013)
- [59] H. Makhlof, M. Weber, O. Messaoudi, S. Tingry, M. Moret, O. Briot, R. Chtoutou, M. Bechelany, *Appl. Surf. Sci.* **426**, 301 (2017)
- [60] T. Zhai, B. Liu, C.H. Ding, L.X. Lu, C. Zhang, K.G. Xue, D.A. Yang, *Surf. Coat. Technol.* **272**, 141 (2015)
- [61] Y. Tai, H. Chen, C. Xu, Y. Liu, *Mater. Lett.* **171**, 158 (2016)
- [62] R. Zhou, H. Chen, C. Xu, X. Hou, G. Liu, Y. Liu, *J. Mater. Sci. Mater. Electron.* **26**, 3530 (2015)
- [63] Y.H. Chou, Y. Sung, C.Y. Bai, M.D. Ger, *J. Electrochem. Soc.* **155**, D551 (2008)