



Semiconducting and electrical properties of thin hybrid films from pyrrolyl- and anilnyl-silicon precursors

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HIGHLIGHTS

- OH- π interactions govern the semiconducting behavior of the hybrid films.
- Cu⁺ (π -ligand) coordination influences the electrical properties markedly.
- Semiconductivity and Cu- π (N) complexation determine the buried interface stability.

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ABSTRACT

The semiconducting and electrical properties of as-deposited and ex-situ irradiated hybrid films on FTO and enriched in Cu 2024-T3 Al alloy substrates, using hydrolyzed solutions of pyrrolyl- (PySi) and anilnyl-silicon (AnSi) compounds, were investigated by means of photocurrent (PCS) and electrochemical impedance (EIS) spectroscopies. AnSi based film is p-type semiconducting while PySi is n-type due to OH- π interactions and charge pinning by silanol (SiOH). The electrical properties depend on the extent and nature of donor-acceptor complexes developed in solution, as well as on the propensity towards Cu⁺ (π -ligand) coordination during the surface treatment step. The aniline derivative is more prone to Cu- π (N) complexation, which imparts stability to the buried interface. This, however, turns reactive in the presence of aggressive Cl⁻ due to displacement reactions as the penetration of these species throughout the p-type semiconducting AnSi films is facilitated, contrariwise to the n-type PySi film.

1. Introduction

Anilnyl- and pyrrolyl-silicon derivatives (Fig. 1) as precursors of hybrid films to protect Al alloys against corrosion in chloride containing solutions have been widely investigated by our group [1–9]. Films with transparent appearance and thicknesses of 2–5 μ m are typically obtained by direct-to-metal surface treatment with hydrolyzed methanol-based solutions of PySi and AnSi. The hybrid films behave as “reservoir” (polysiloxane chains) of a “corrosion inhibitor” (aniline or pyrrole moieties), which acts against metal substrate degradation as siloxane linkages fail by back hydrolysis [1–5].

Hydrolyzed structures of PySi are stabilized by OH- π interactions between electron-rich pyrrole ring and electron-deficient silanol group (SiOH) [1,2,6,9]. Electropolymerization on inert substrates leads to hybrid films with mixed n-p doping behavior regardless the extent of hydrolysis [7–9], indicating that OH- π donor-acceptor complexes and the charge pinning action on pyrrole (Py) ring by silanol (SiOH) are preserved in the hybrid network. OH- π interactions are less effective

with the more basic AnSi, which promotes deprotonation and self-condensation of SiOH [3–5,8,9]. The p-type redox behavior of electrogrown films involves anion and proton exchange [8,9], as typically obtained for polyaniline and derivatives [10,11]. Protonation/deprotonation is more likely to involve semiquinoid/benzenoid aniline structures (N–H \cdots N) [9]. The electroactivity of the hybrid films supports the shift of oxygen reduction reaction (ORR) to the film/solution interface in aggressive Cl⁻ environment. The better barrier action of PySi films could be justified by the mixed n-p type redox behavior, limiting the penetration of Cl⁻ through the film thickness towards the metal/film interface [1–5]. Nonetheless, the labile protons of aniline moieties bring about a buffer effect on local alkalization produced by the ORR [4,5]. In addition, the delocalized but not involved in the aromatization lone pair of electrons on the N atom, and the strong specific orbital Cu- π (N) interactions [12] make the metallo-complexation particularly relevant in the case of Cu-rich Al 2024-T3 [5], leading to a decrease of Al-Cu microgalvanic coupling [4].

Solid state photoactive behavior of the hybrid films has been

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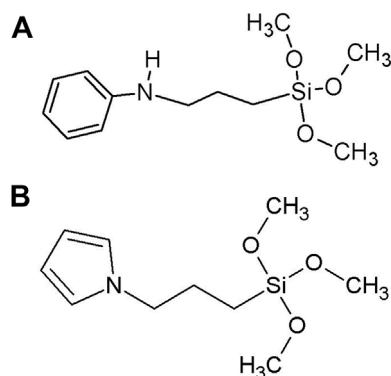
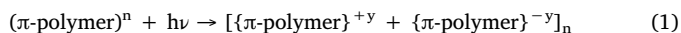


Fig. 1. Schematic structures of (a) anilnyl-silicon and (b) pyrrolyl-silicon derivatives.

indicated in Ref. [5]. In particular, AnSi and PySi films on different Al alloys turned red-brown, and then progressively discolored during exposure to natural light, in correspondence with the increase and the decrease, respectively, of the absorption tail at wavelengths below 450 nm as monitored by solid UV–vis spectroscopy. These findings point to light-induced photoexcitation of pyrrole and aniline moieties within the hybrid network, promoting redox conversion reactions that alter the doping level. Differently from (electro)chemical doping, where permanent electrical conductivity lasts until the charge carriers are purposely removed, photoconductivity lasts until charge carriers are trapped or decay back to the ground state. The generation of free charge carriers by local oxidation and nearby reduction of conducting polymers has been represented by the general equation [10]:



where y is the number of electron-hole pairs. The fact that surface discoloration was less important for the hybrid films deposited on Al 2024-T3 [5], in particular for the case of PySi films, suggests that copper species act as redox promoters and favor charge trapping.

In this work, photocurrent spectroscopy (PCS) and electrochemical impedance spectroscopy (EIS) were used to investigate the semi-conducting and electrical properties of AnSi and PySi hybrid films deposited on FTO and enriched in Cu Al 2024-T3 substrates. The effect of controlled white light irradiation was studied in parallel. In addition to methanol-based hydrolyzed solutions of the silicon derivatives (Fig. 1) [1–5,8], treatment solutions containing non-HAP, low-VOC and biodegradable methylacetate in excess were used for surface modification of Al 2024-T3.

2. Experimental part

2.1. Materials and reagents

The materials used were glass slides (50 mm × 50 mm × 2.2 mm) of fluorine doped tin oxide (FTO) ($\approx 7 \Omega/\text{sq}$, Aldrich) and metallic specimens (20 × 30 × 1.5 mm) made from a commercial wrought sheet of 2024-T3 Al alloy (Aviometal Spa) with nominal composition (wt. %) 4.67Cu – 1.34Mg–0.63Mn – 0.25Fe – 0.15Si, bal. Al. Unless otherwise specified, all solutions were prepared with commercially available reagent grade substances and solvents. Aqueous solutions were prepared using water of MilliQ quality.

2.2. Enrichment in Cu of Al 2024-T3

Before use, Al 2024-T3 surfaces were wet-ground up to 800 grit with abrasive SiC paper, cleaned in ethanol, and artificially enriched in Cu, according to a reported procedure [13]. Briefly, metallic specimens were immersed in 1.5 g/L NaOH solution for different times (t_{etch} up to

30 min), rinsed in large amounts of water and dried with hot air. The enrichment in Cu was verified by cyclic voltammetry (CV) in pH 8.4 borate buffer solution (8.17 g/L $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ + 7.07 g/L H_3BO_3), using as-abraded pure Cu (99.99%) as reference material [13]. The corrosion behavior was evaluated in 0.6 M NaCl by electrochemical impedance spectroscopy. Further experimental details and results are provided as supplementary information (Figs. S1, S2 and Table S1). For the alkaline etching time of 5 min, the enrichment in Cu of the surface was significant while the consequent increase of surface roughness was negligible in comparison to higher etching times as no capacitive currents at $E > +0.1$ V (vs Ag/AgCl) were recorded (Fig. S1). In addition, the impedance response differed less from that of the as-abraded substrate (Fig. S2, Table S1), indicating little contribution of flaws on the mixed Al-Cu (hydr)oxide layer that are promoted with prolonged alkaline etching [13]. For this condition, enhanced corrosion rather than inhibition and steric hindrance effect slowing down diffusion of corrosion products was indicated [14]. Accordingly, $t_{\text{etch}} = 5$ min was used for the enrichment in Cu of Al 2024-T3 surfaces prior to modification with silanes.

2.3. Hybrid films deposition

Hydrolyzed solutions of silicon derivatives (Fig. 1), namely N-[3-(trimethoxysilyl) propyl] aniline (AnSi) and N-[3-(trimethoxysilyl) propyl] pyrrole (PySi) were prepared at 4 vol% in solvent mixtures made of either methanol and water (MeOH/ H_2O 95:5) or of methyl acetate, ethanol and water (MeOAc/EtOH/ H_2O 50:25:25). The pH was adjusted to 4 with acetic acid. Solutions were allowed to stand for 3 days for hydrolysis to occur. The typical pink and orange-brown colors of MeOH based solutions of AnSi and PySi [1–5,8,9] were less intense in the solvent mixture containing polar, aprotic MeOAc in excess, indicating less favored formation of OH- π and N-H \cdots N agglomerates [9]. In the following, treatment solutions are identified by the solvent in excess.

Surface modification of enriched in Cu Al 2024-T3 was carried out as in previous works [1–5,8]. Metallic specimens were preheated at 120 °C for 10 min, immersed in a given silane hydrolyzed solution for 3 min, and finally placed in an oven at the temperature indicated above for 1 h. The same procedure, excluding the pre-heating step, was used for the surface modification of FTO substrates. Unless otherwise specified, ex-situ irradiation with white light was carried out under air (O_2) atmosphere for 2 h, using a 450 W Xenon lamp (Newport) with maximum excitation range between 400 and 700 nm. Gold-colored surfaces resulted more evident with enriched in Cu in Al 2024-T3.

2.4. Photocurrent spectroscopy (PCS) experiments

Substrates treated with PySi and AnSi solutions containing MeOH in excess were used. The modified electrode was positioned vertically in a one-compartment electrochemical cell containing 0.1 M LiClO_4 in propylene carbonate (PC), a Pt wire as a counterelectrode, and Ag/AgCl as a reference electrode. The monochromatic irradiation of the working surface through the cell quartz window was provided by a 450 W tungsten lamp (Muller) coupled with a monochromator (Kratos). Photocurrent (I_{ph}) spectra were recorded at constant potential of -1 V (Ue) and irradiating wavelengths λ from 250 to 450 nm at intervals of 5 nm, using a PAR 5206 lock-in amplifier interfaced with a computer and locked to a mechanical chopper (frequency of 13 Hz) to separate I_{ph} from the total current circulating in the cell. The variation of I_{ph} with time during dark/light cycles was recorded for excitation λ between 280 and 400 nm in the presence of O_2 . I_{ph} data were corrected for the efficiency of the lamp–monochromator system at each wavelength. For selected conditions, cyclic voltammograms between 0.0 and 0.6 V (vs Ag/AgCl) in 0.25 M Na_2HPO_4 (pH 8.4) were recorded using the electrochemical system indicated above and a computer driven PARSTAT 2263 potentiostat. For some conditions, ex-situ irradiation and

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