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Cathodic Deposition of Silicon from Phenyltrichlorosilane in an Organic Solvent

Ali H. Abbar[1,*] *and Sameer H. Kareem*[2]

[1] Chemical Engineering Department, College of Engineering Al- Qadessyia University, Iraq.
[2] College of Science for Women, Baghdad University, Iraq.
[*]E-mail: aliha68@yahoo.com

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The electrodeposition of silicon was carried out in acetone containing phenyltrichlorosilane and tetrabutylammonium chloride. Linear sweep voltammograms showed the possibility of electrodeposition of Si at −3.3V versus Pt quasi-R.E using a variety of cathode substrates including copper, brass, aluminum, stainless steel, titanium and amalgamated copper. Titanium and amalgamated copper electrodes have been given the highest current at the center of reduction wave. Potentiostatic electrolysis yielded porous deposit at −3.3V using titanium or amalgamated copper substrates. EDX results indicated that the electrodeposited Si was so active that it was oxidized immediately in the air. The AFM picture and granularity distribution chart for silicon film on titanium cathode showed that the silicon deposit is amorphous because the lateral extension of the finer corrugation is within the range of sizes expected for quantum wires. While no amorphous silicon can be obtained on amalgamated copper cathode in spite of giving higher current at the wave reduction approaching to that obtained on titanium substrate.

Keywords: silicon electrodeposition, Non-aqueous solvent, amorphous silicon, amalgamated copper electrode, phenyltrichlorosilane, Quaternary ammonium salt.

1. INTRODUCTION

Amorphous silicon is a semiconductor material displaying optical and electronic properties highly favorable to photoconductive and photovoltaic applications; these favorable properties have been generally attributed to the presence of an appropriate content of hydrogen within the film. Thus, Amorphous silicon (a-si) is a promising new material for the fabrication of low cost large area solar cells of medium efficiency[1].It is usually made by glow discharge decomposition of silane[2], by thermal decomposition of silane[3] , by sputtering[4],or by sublimation of silicon[5].Such processes require substantial equipment expenditures, employing sophisticated vacuum technology methods for thin film deposition[6] .

An alternative method for preparing (a-si) is the electrochemical deposition which is a low cost energy efficient method as required for the manufacture of low cost solar cells. It is attractive for various reasons: it is easy to regulate the hydrogen content of (a-si); it does not involve vacuum equipment or furnaces and is therefore convenient ; doped material can be made by adding compounds of the dopant to the electrolyte[7] .

As is well known, silicon cannot be electrodeposited from aqueous electrolytes because of hydrolysis of its salts and very large negative potentials required for oxygen[8].The electrodeposition of silicon from a fused salt requires electrolyte temperatures in excess of about 450°C and high as 800°C, such temperatures induce the formation of crystalline as opposed to amorphous silicon. Also the high temperature introduce problem of formation the silicides. There is also considerable opportunity for impurities to diffuse into the silicon [9-17].

Amorphous silicon has been prepared by electrochemical reduction using a non – aqueous electrolytic solution containing solute of silicon halide soluble in an aprotic organic solvent under cover of an inert gas. Different types of solute, organic solvents, supporting electrolytes and cathode materials have been studied in previous works [18-26]. The preferred solvents were tetrahydrofuran / benzene, tetrahydrofuran / toluene, dioxolane / benzene, and dioxolane/toluene. Silicon tetrachloride or trichlorosilane were used as solute and tributylammonium perchlorate as a supporting electrolyte. Platinum, molybdenum and nickel were used as cathode. The deposited film visually appeared generally golden brown in color with multi – color overtones. Silicon electrodepoition has been recently tried in ionic liquids [27-34].

The previous works have not been used phenyltrichlorosilane as a source of silicon in spite of using different types of silicon compounds. On the other hand, phenyltrichlorosilane is the second silicon compounds which produced on a commercial scale so utilizing it for producing silicon is a promising step. The present research is conducted to investigate whether or not amorphous silicon deposits can be obtained using phenyltrichlorosilane as a silicon source. The silicon electrodeposition is achieved using six different materials of cathode. The electrodeposition process of Si film is discussed on the basis of polarization curves and surface structure of the deposits using EDX and Atomic Force Microscopy.

2. EXPERIMENTAL WORK

All experiments were carried out under an argon atmosphere at room temperature. As a working electrode: copper ,brass, aluminum ,stainless steel, titanium and amalgamated copper rods (5mm in diameter and 80mm in length) were used in linear sweep voltammetry studies. Titanium and amalgamated copper plates (10mm×50 mm) were used as cathode in potentiostatic electrolysis. Platinum wire (0.5mm in diameter) coated by a heat shrink tube was employed as a quasi-reference electrode. Graphite pot was used as a counter electrode. The amalgamation of copper electrode was achieved by chemically depositing mercury from a 2% mercuric sulphate solution in 5% sulfuric acid for 5 min [35].Electrode surfaces were mechanically polished to a mirror finish then ultrasonically cleaned in deionized water for 3 min, and then rinsed out with deionized water, ethanol, and acetone. Platinum wire was ultrasonically washed in water with detergent for 20 min and subsequently washed in deionized water before assembling the electrolytic cell.

The electrolytic cell used in the experiments consisted of two parts: graphite pot (50mm in diameter and 60mm in length) and cover made from polytetrafluoroethylene (PTFE) as shown in Figure 1. The cover provided with inlet and outlet Teflon tubes for charging and discharging of Argon gas. The inlet tube was connected internally with ceramic tube (5 mm in diameter and 40mmin length) for bubbling argon gas .The working electrode was enclosed by Teflon screwed tube fixed at the center of cell cover. This assembly provides the mean to lowering and raising the cathode inside the electrolyte to the desired level.

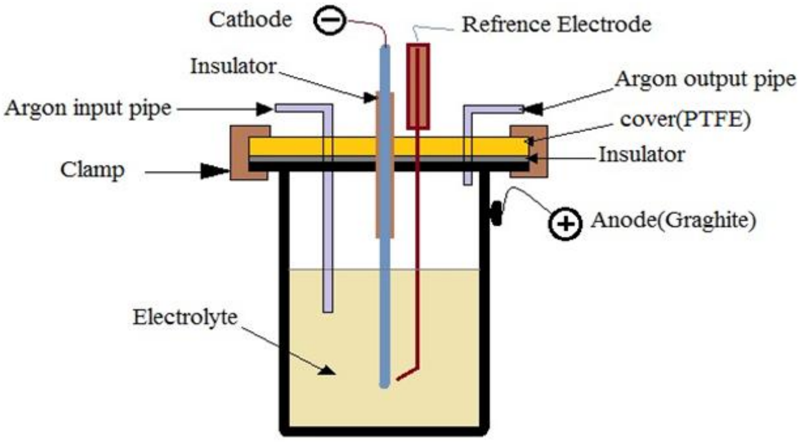


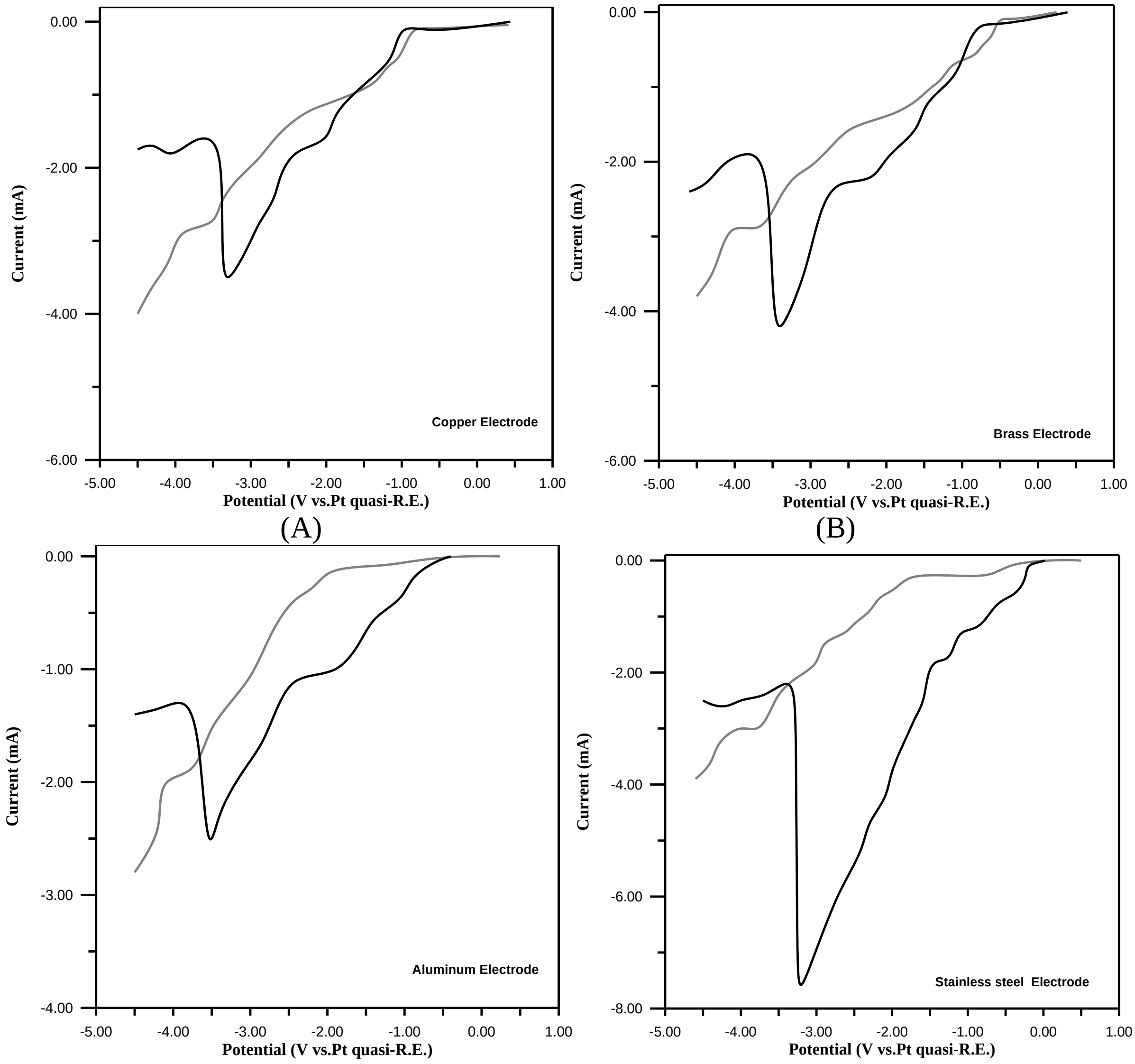
Figure 1. The electrolytic cell

Phenyltrichlorosilane (Sigma-Aldrich, ≥97.0%) was added to the organic electrolyte as a Si source. Acetone (Fluka ,puriss. p.a., absolute, ACS reagent, ≥99.5% GC) was chosen as a non-aqueous solvent. These two chemical reagents were used as received. The electrolyte solution containing phenyltrichlorosilane and acetone, however, showed a poorer conductivity. Thus, tetrabutylammonium chloride (Fluka, for ion pair chromatography, ≥99.0%) was added to the electrolyte solution as a supporting electrolyte. The composition of supporting electrolyte was adjusted to 0.07M TBACl in acetone. The phenyltrichlorosilane then added to obtain the required concentration level. Water content in electrolyte solution measured by Karl Fischer coulometric titration was less than 10 ppm.

Electrochemical measurement was carried out using a model 273 A potentiostat/galvanistat system controlled by electrochemical 270/250 software (both from GE&G Princeton applied research corporation. The polarization was achieved at scan rate 10mV/s. The electrode potential reported in this paper was measured or set relative to the potential of Pt quasi-reference electrode. All samples produced by potentiostatic electrolysis were immersed in acetone and kept under argon gas. The samples were characterized by energy dispersive X-ray (EDX, kevex) for determining their purity .The morphology of deposits was investigated by using Atomic Force Microscopy (AA3000, Angstrom, USA).

3. RESULTS AND DISCUSSION

3.1. Linear sweep Voltammetry

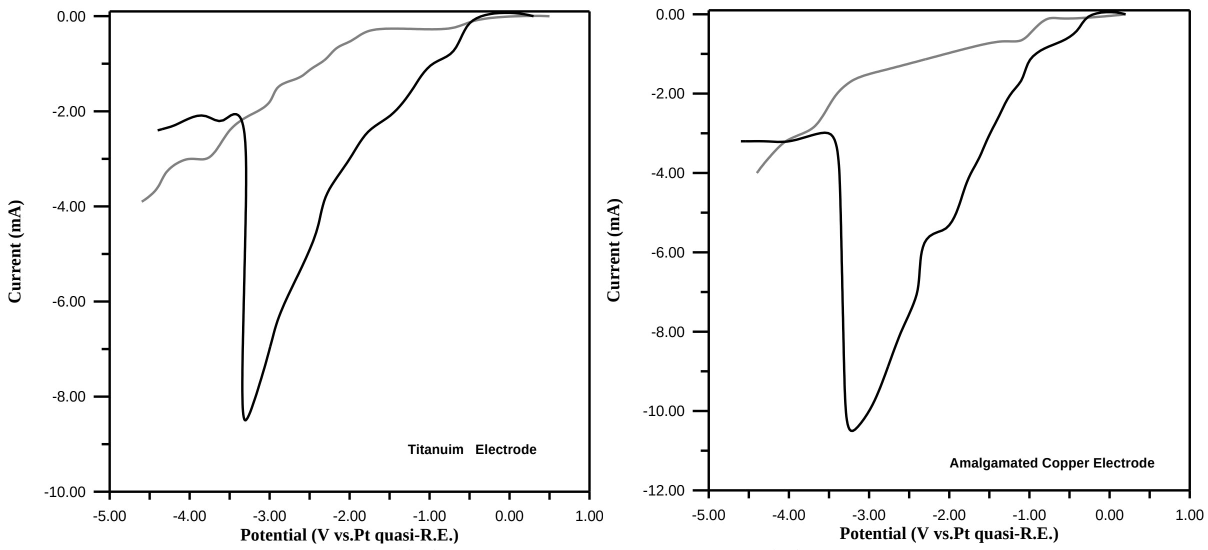


(A) (B)

(C) (D)

Figure 2. Linear sweep voltammograms of 0.6M phenyltrichlorosilane –0.07M TBACl–acetone electrolyte (black curve)and in 0.07MTBACl–acetone electrolyte (gray curve).Scan :10mV/s (in both case):A)Copper, B)Brass, C)Aluminum, D)Stainless steel(316)

Linear sweep voltammetry was performed to examine the reduction potential of phenyltrichlorosilane . Figures (2 -3)show the linear sweep voltammograms for reduction of phenyltrichlorosilane on copper, brass, aluminum, stainless steel, titanium, and amalgamated copper electrodes in acetone containing 0.07M TBACl with 0.6M phenyltrichlorosilane (black curve) and without phenyltrichlorosilane (gray curve). Comparison between these curves indicates that a reduction wave centered at −3.3V (vs.Pt.quasi-R.E) appeared only in case of the electrolyte containing phenyltrichlorosilane.



(A) (B)

Figure 3. Linear sweep voltammograms of 0.6M phenyltrichlorosilane –0.07M TBACl–acetone electrolyte (black curve)and in0.07M TBACl–acetone electrolyte(gray curve).Scan rate :10m V/s(in both case):A)Titanium ,B)Amalgamated copper electrode

It suggests that phenyltrichlorosilane should be reduced around this potential. The presence of only a strong single peak suggests that the reduction of phenyltrichlorosilane is essentially a one-step process according to the following suggested cathodic deposition of silicon:

$$Si^{+4} + 4e^{-} \longrightarrow Si$$

To characterize the behavior of these polarization curves, four potentiostatic experiments were achieved at -2.5,-3.0,-3.3and-3.6V cathodic potentials respectively for the same operation time (1hr.).At -2.5V, the results indicate no silicon deposits are formed but the color of solution is changed from transparent to pale brown .This is an indication of the reductive decomposition of TBA^{+} species in acetone electrolyte accompanied with the decomposition of impurities such as H_2O or HCl. The operation at -3.0 V gives also no deposits of silicon but with a deep brown color of solution. This may be interrupted as further decomposition of solvent and supporting electrolyte .This behavior is supported by Nishimura and Fukunaka[26] where the chronopotentiogram shows the reductive reduction of TBA^{+} at -2.7V.

At -3.3V, 20µm silicon deposits are obtained with pale brown color of solution .This result refers to the reduction of silicon as the main reaction accompanied with slowly decomposing of electrolyte. This behavior is supported by a single peak in the polarization curve at this potential. Dark spongy silicon deposits are formed in addition to gas evolution occurs when the cathodic potential is -3.6V.The spongy structure of silicon at this cathodic potential may be result from the penetration of hydrogen gas through the deposits.

It is cleared that each of stainless steel, titanium and amalgamated copper electrodes give approximately the highest current at the center reduction wave (-3.3V vs.Pt.quasi-R.E), approximately twice that obtained in the other electrodes as shown in Table 1 for the same reduction potential. Titanium electrode gives the highest current (8.5mA) therefore it is preferred as an electrode material for reduction of phenyltrichlorosilane . Nishimura and Fukunaka [26] found that the reduction wave of $SiCl_4$ occurred at -3.6V (vs.Pt.quasi-R.E) while Agrawal and Austin [20] found that the reduction wave of $SiHCl_3$ located at -2.3V (vs.Pt.quasi-R.E) .In the present work, reduction wave of phenyltrichlorosilane is located at-3.3V.This may be resulted from the effect of phenyl group which shifting the reduction wave toward the more negative potential than that for the reduction of $SiHCl_3$.

Table 1. Current at the center of reduction wave for phenyltrichlorosilane at -3.3Vvs.Pt.quasi-R.E.

Cathode material	Current (mA)
Aluminum	2.68
Copper	3.82
Brass	4.25
Stainless steel	7.8
Amalgamated copper	8.4
Titanium	8.5

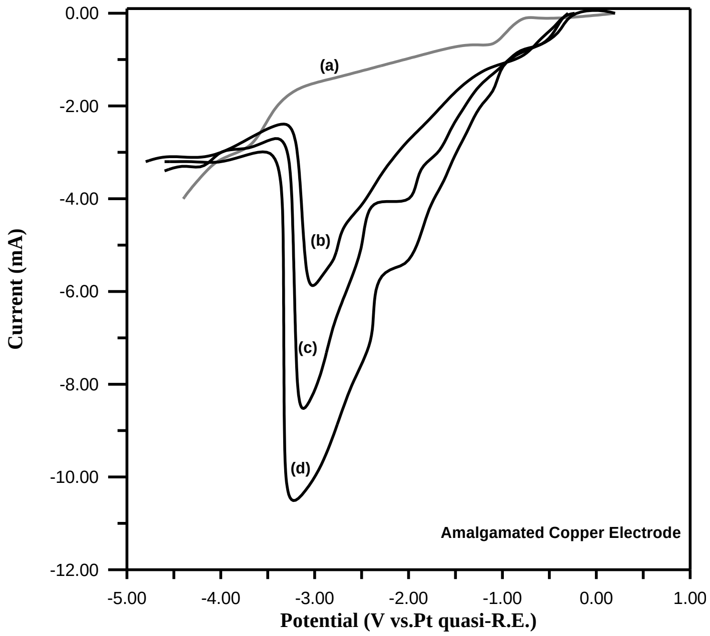


Figure 4. Linear sweep voltammograms of phenyltrichlorosilane in TBACl–Acetone electrolyte: a) without phenyltrichlorosilane, b)0.3M ,c)0.6M, d)1.2M. Scan rate: 10m V/s

The effect of phenyltrichlorosilane concentration on the polarization curves using amalgamated copper electrode is shown in Figure 4 where higher concentration gives higher current at the center of reduction wave, however increasing phenyltrichlorosilane concentration higher than (0.6M) leads to increasing the decomposition of acetone where the color of solution becomes more brown in addition to increasing the total voltage of cell from 7.0V to 9.5 V, therefore it is preferred to operate at concentration equal or lower than 0.6M .

3.2. Potentiostatic Electrolysis

The potentiostatic electrolysis was conducted in electrolyte containing 0.6M phenyltrichlorosilane dissolved in 0.07M TBACl –Acetone supporting electrolyte at −3.3V (vs.Pt.quasi-R.E) for operation time(4 hr.) using titanium and amalgamated copper electrodes. The total voltage of the cell in the potentiostatic operation using amalgamated copper electrode was 7.0V while for operation using titanium electrode was 6.3V. The color of solution at the end of each experiment was brown which result from the decomposition both of acetone and quaternary ammonium cation. The weights of deposits at the end of potentiostatic operation are 0.12g and 0.096g on titanium and amalgamated copper electrodes respectively leading to columbic efficiency of 87%and 81%respectivly.

3.3. EDX of silicon deposits

The EDX analysis of silicon deposit obtaining via potentiostatic operation on titanium substrate is shown in Figure 5.The analysis demonstrates that the deposit consists of Si, O, and Cl. Oxygen might be derived from the oxidation in the air, as mentioned by other researchers [25, 36].The high reactivity of the electrodeposited silicon with oxygen might be attributed to its porous structure and rapid diffusion of oxygen into it.

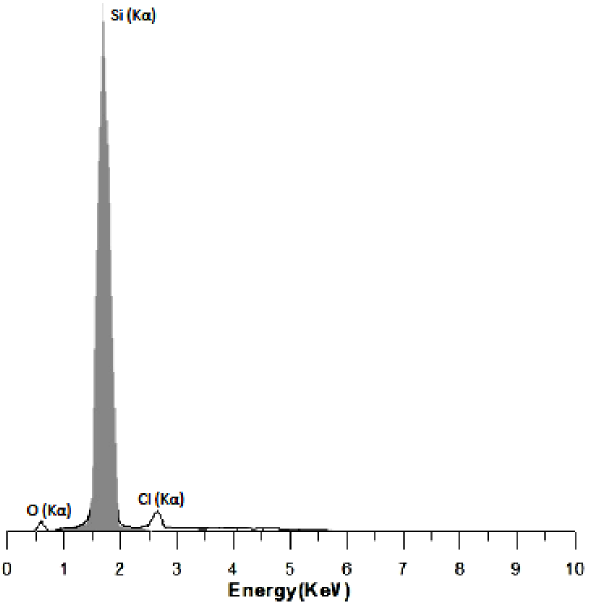


Figure 5. EDX spectrum for the sample electrodeposited at −3.3V (vs.Pt.quasi-R.E) for (4 hr.)potentiostatic operation on titanium cathode

3.4. Atomic Force Microscopy results

Figures (6 and 7) show the AFM picture and granularity distribution chart for silicon deposits on amalgamated copper and titanium cathodes respectively. The lateral extension of hills for film depositing on amalgamated copper is approximately 18.5nm while that on titanium is 46nm.A finer corrugation is superimposed on the structure of the deposit on titanium substrate while large corrugation on amalgamated electrode .The average particle size for the two deposits is in the range (160-165nm).The lateral extension of the finer corrugation on titanium substrate is within the range of sizes expected for quantum wires [37]. This observation is compatible with the assumption that such structure on titanium substrate is covered with an amorphous surface layer of silicon deposits. For the present purposes, the deposited material is therefore considered to be amorphous on titanium substrate rather than amalgamated copper substrate.

In spite of amalgamated copper electrode gives higher hydrogen overvoltage which makes it suitable for many organic reduction reactions [38], amorphous silicon cannot be obtained from this material. The reason may be attributed to the surface morphology of amalgamated copper causing a crystalline not amorphous structure of silicon deposits.

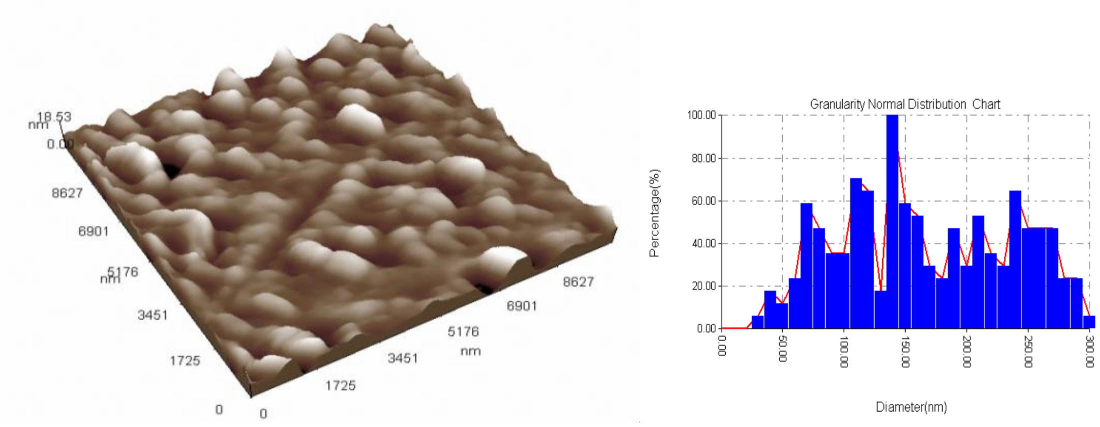


Figure 6. AFM image and granularity normal distribution chart of silicon film on amalgamated copper electrode under potentiostatic operation at-3.3V (vs.Pt.quasi-R.E)average particle size=161.05 nm

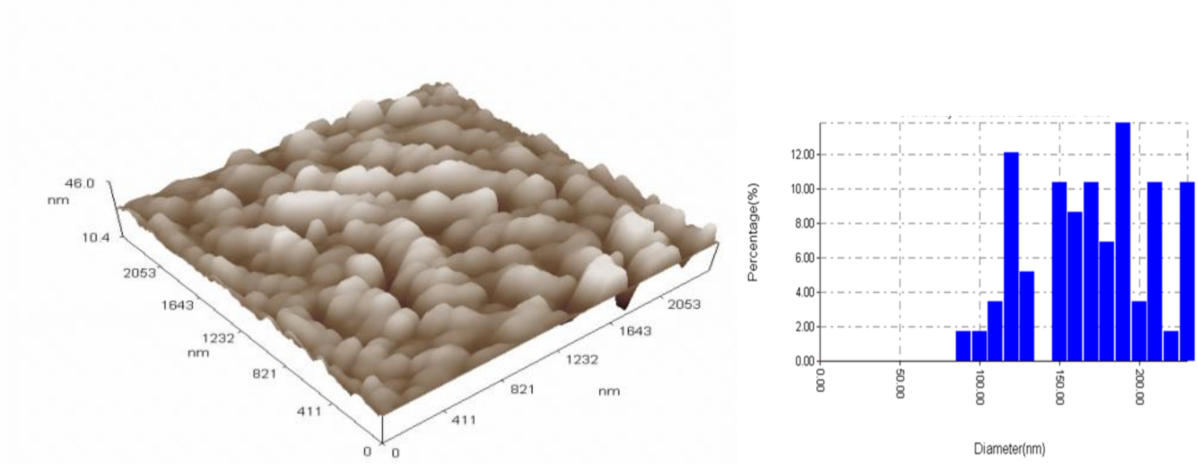


Figure 7. AFM image and granularity normal distribution chart of silicon film on titanium electrode at-3.3V (vs.Pt.quasi-R.E), average particle size=164.74 nm.

4. CONCLUSIONS

The electrodeposition of silicon was successfully accomplished on cathodes of copper, brass, aluminum, stainless steel, titanium and amalgamated copper in acetone solvent containing 0.6M phenyltrichlorosilane and 0.07M TBACl. The peak of silicon reduction occurs at −3.3V (vs.Pt.quasi-R.E) which is higher than that obtained by reduction of $SiHCl_3$ [20] and lower than that obtained by reduction of $SiCl_4$ [26]. The results show that amalgamated and titanium electrodes give higher current at the beak of reduction wave. The silicon deposits are highly sensitive to oxygen due to its porosity therefore it should be protected by inert solvent such as acetone before using. Amorphous porous deposit can be obtained only on titanium cathode by potentiostatic electrolysis for 4 hr. at −3.3V(vs.Pt.quasi-R.E),while no amorphous silicon can be obtained on amalgamated copper electrode in spite of its higher current at the reduction wave, therefore titanium is a promising material for preparation amorphous silicon from phenyltrichlorosilane as silicon source .A further investigation may be conducted for comparison the results of present work with deposits that may be obtained from reduction of $SiCl_4$ or $SiHCl_3$ using the same cathode and solvent of the present work. A step in this direction is promising.

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