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Implimentation of Computer-controlled Electrodeposition methodology for Depositing Metal Oxide Thin Films

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Abstract

Metal-oxide thin films (ZnO, TiO_2 and other so on) have received considerable interest from scientists due to their remarkable performance in electronics, optics and photonics. In this study we have reported a way of fabricating films applying different conditions in a computerized way where PC has been interfaced with Keithley 2400 Source Measure Unit (SMU) with Lab-view software and controls the electrodeposition mechanism either in a voltage or current controlled way. The potential difference between the electrodes, current flow and resistivity of the electrolyte, duration of deposition of molecule on the substrate and their corresponding features as well as curves (I-V, R-V and I-T) become visible in the computer monitor using 'LabVIEW' software. Additionally, we fabricated ZnO films on Fluorine Doped Tin Oxide (FTO, SnO_2:F) substrate from an electrolyte of metallic-salt [$Zn(NO_3)_2$]. Almost precise potential difference of 0.718V (DC) was provided by Keithley 2400 Source Measure Unit between the working electrode and counter electrode of a zinc nitrate electrolyte [0.5M of $Zn(NO_3)_2$ solution; 0.0125:1.375 = zinc nitrate : water (molar weight)] resulting in a smooth deposition of metallic oxide on FTO substrate. I-V, R-V and I-T curves have been analyzed to prove the already built ZnO formation mechanism. Both the as-deposited and annealed films stance with semi-conductive behavior where a marginal differences in resistivity exist between this two.

Keywords: *Electrodeposition, KEITHELY source measure unit, LabVIEW, FTO, ITO, Coating.*

1. Introduction

At present century huge population, advanced industrialization, rising number of hunger demands immense power to meet those challenges around the world. In the 20th century, people developed so many techniques and methods for producing and distributing power from solar system, but most of these methods were costly as well as inefficient and beyond the reach of common people. To make those things better and cost effective people developed so many ideas, application of thin films on solar cell is one of them, it not only increase efficiency of solar cell but make it cost effective and versatile for applying different purposes [1].

Today electrodeposition method has been received a great attention due to its fidelity for fabricating high standard nano-structured thin-films of different metal oxides such as ZnO [2-5], Cu_2O [6-8], TiO2 [9] and other so on. Electrodeposition technique [10] has the following advantages (I) thickness and morphology of films can be precisely controlled by adjusting electrochemical parameters such as current or potential, (II) uniform and compact thin-films can be synthesized either on substrates of complex shapes or in column shaped material, (III) higher deposition rates can be easily obtained over conventional processing. Since deposition on substrate takes place at the rate of current flowing through the circuit and potential applied to the electrodes, this method facilitates both the current controlled and voltage controlled deposition on the substrate, which is accomplished by "2400 KEITHLEY Source Measure unit" without resulting any heat.

ZnO is an n-type semiconductor with a band gap of 3.37 eV and transparent metal oxide. It can be applied in ultraviolet-emitting diodes, piezoelectric devices, electron-field emitters, heterogeneous catalyst for methanol synthesis and short wavelength electro-optical devices [11].

ZnO thin-films was successfully fabricated on different conducting substrates [10, 12-14], in this work, we will explain the computerized electrodeposition methodology in detail and the formation mechanism of zinc oxide [10, 15-17] on FTO substrate utilizing the V-T, R-V, I-T and I-V characteristics.

2. Electrodeposition Set-up

It namely comprises of three parts (fig. 1.): (A) Computerized Controlling Unit, (B) "2400 KEITHLEY source measure unit" and (C) Direct deposition unit.

A. Computerized controlling unit

The following are the supported operating system for PC to drive the basic operation of required software:

i. Windows XP Professional service pack 1 or later
ii. Windows 2000 Service pack 3 or later
iii. Windows NT Service pack 6a or later
iv. Windows 98 Second edition only

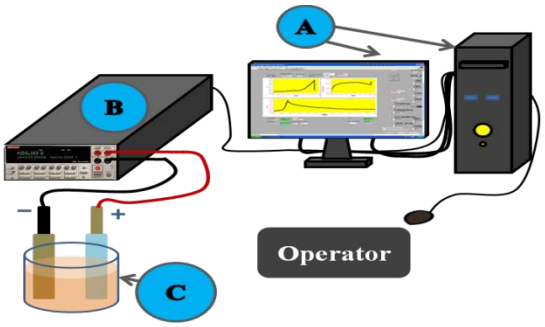

Fig. 1. Visualization of Electrodeposition set-up, (A) Computerized controlling unit, (B) "2400 KEITHLEY source measure unit", (C) Direct Deposition Unit

This unit requires some software and instrument drivers to install for driving the instrument (KEITHLEY) through a automatic controlling process in a computerized way. The required softwares are:

a. GPIB Controller Installation:
To communicate with instrument using GPIB, it needs to install compatible GPIB controller card and associated software drivers in the computer before installing Instrument Drivers. The driver is compatible with the following GPIB controller cards: Keithley Instruments GPIB cards (ISA, PCI, PCMCIA), CEC GPIB cards (ISA, PCI), National Instruments GPIB cards (ISA, PCI, PCMCIA) and INES GPIB cards (PCMCIA)

b. KEITHLEY and INES PCMCIA Controller Installation:
In the case of installing 'INES' driver software we did not install the HP I/O libraries but we selected NI compatibility mode. When installing the INES driver software, if the hardware test fails, it is recommended to change the Interrupt selection to none.

c. Instrument Driver Installation:
There are some other essential drivers in KEITHLEY those were installed correctly.

Use of LabVIEW:

After installing all the drivers LabVIEW was installed. We used LabVIEW to provide input function to the instrument and to illustrate the output mechanism graphically in the computer monitor. The LabVIEW is well suited to "2400 KEITHLEY source measure unit" device. Moreover, to explain the mechanistic origin of deposited material it facilitates I-V, R-V, I-T curves of the direct deposition unit, additionally LabVIEW accommodates Offset voltage, Voltage step, Timer action and current offset for precise and accurate application of current and voltage to the working stage. The step wise data of different parameters (voltage, current and resistance) are stored in the specified directory as text when operator presses the end switch.

B. 2400 KEITHLEY source measure unit:

Keithley's Series 2400 Source Measure Unit (SMU) Instruments are designed specifically for test applications that demand tightly coupled sourcing and measurement. All Source Meter models provide precision voltage and current sourcing as well as measurement capabilities. Each Source Meter SMU instrument is both a highly stable DC power source and a true instrument-grade 6½-digit multimeter. The power source characteristics include low noise, precision, and readback. The multimeter capabilities include high repeatability and low noise. The result is a compact, single-channel, DC parametric tester. In operation, these instruments can act as a voltage source, a current source, a voltage meter, a current meter, and an ohmmeter.

C. Direct Deposition Unit:
It is mainly demanded by two basic parts the first one is electrolyte, second one is Electrodes. Electrolyte depends on what material is going to be deposited on substrate. Electrodes are of three types (i) working electrode, (ii) counter electrode and (iii) reference electrode. Normally deposition takes place on working electrode. Conventionally reference electrode is used in the purpose of fixing the voltage and current precisely, as we have employed "2400 KEITHLEY source measure unit" so it is optional in our study. There are two types of deposition one is cathodic deposition and another is anodic deposition, depending on the deposition process the substrates are specified to the electrodes. In our study we maintained a cathodic deposition.

3. Experimental Detail

ZnO was electrochemically deposited on FTO substrate. Prior to experiments, firstly the FTO quartz crystal has ultrasonically been cleaned with 99% ethanol solution for 15 minutes in order to remove organic residue and then ultrasonically cleaned with distilled water for 5 minutes, finally it has been rinsed thoroughly with distilled water and dried using air compressor for three minutes. Beakers have been cleaned with 75% nitric acid (HNO_3), then with 95% ethanol and then thoroughly cleaned with distilled water.
To maintain the same concentration of solution zinc sheet has been used as counter electrode to provide Zn^{++} ion in the solution. FTO has been arranged as working electrode on which deposition takes place and both the electrodes are placed 1.5cm apart in the solution. 0.5M solution of $Zn(NO_3)_2$ has been prepared with ultra-pure water and stirred for 15 minutes, the whole experiment has done in room temperature.
Electrodeposition has been executed at constant potential of 0.72V using 2400 KEITHLEY source measure unit for 10 minutes, the current-voltage characteristic of the solution has been measured in a computerized way using LabVIEW and all the data have been stored as text for further analysis of the experiment. I-V, R-V, V-T and I-T curves founded in the experiment have been analyzed for understanding the formation mechanism of ZnO on FTO substrate.

4. Result and Discussion

Current vs Voltage(I-V), Current vs Time(I-T) and Resistance vs Voltage(R-V) curves commence to be visible on the computer monitor when completing whole circuit a direct commend via labVIEW is provided to start. It works in two ways (i) Sourcing Unit and (ii) Measuring Unit.

In Sourcing Unit the decimal input of voltage/current is suitably converted into binary format so that this signal becomes compatible to GPIB driver. GPIB driver compatible for both instrument as well as PC works to communicate between them. GPIB driver conveys those signals to KEITHLEY 2400 to develop a voltage/current source of prescribed amplitude. The block diagram is shown below (fig. 2.):

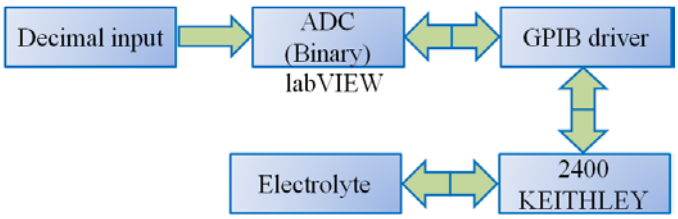

Fig. 2. Block diagram of Sourcing Unit.

In sourcing unit labVIEW stores the fixed magnitude of input value by letting it expands comparing with instrument output from zero, when instrument output acquires the prescribed value as input it continues running towards definite time keeping all the magnitude of compared inputs stored.

In measuring unit KEITHLEY 2400 measures the time varying impedance between output ports as well as current through loads along with supplying as a sourcing unit (voltage), when it works as a current source, it measures impedance and potential difference.

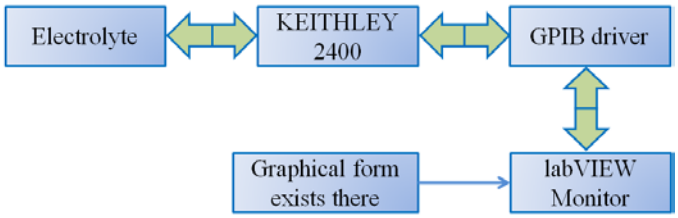

Fig. 3. Block diagram of Measuring Unit.

Current through two electrodes (two output ports of instru-ment) and impedance between two electrodes are measured and measuring data are sent to the labVIEW monitor via GPIB driver by KEITHLEY 2400 (fig. 3.). Subsequently data storing and portraying functions take place in LabVIEW section.

$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$, ---------- (1)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, ---------- (2)

$Zn^{2+} + OH^- \rightarrow Zn(OH)^+$ /FTO, ----------(3)

$Zn(OH)^+$/ITO + $OH^- \rightarrow ZnO$/FTO + H_2O, ----------(4)

These conventional equations reveal how ZnO gets deposited on a substrate. At the beginning the nitrate ions, water travelling around cathode and electron from cathode come close together to form nitrous ion and hydroxyl ion (eq-1), if the solution is oxygen saturated then travelling oxygen, water and electron from cathode form additional hydroxyl ions (eq-2) relentlessly in the solution and increase pH of the solution as well as cathode (FTO). Proportion to the number of electrons get released for producing hydroxyl ions, Zn^{2+} ions get rid of Zn sheet located at anode and affiliate to the existing hydroxyl ions in the solution to form zinc hydroxide ion [$Zn(OH)^+$] (eq-3). Finally, positively charged zinc hydroxide [Zn(OH)+] ions attract to the negatively charged cathode where hydroxyl ions exist due to higher pH of substrate, then according to eq-4, ZnO is formed with different structure on the substrate (FTO) and H_2O release in the solution, this process repeats cyclically. When ZnO grows on the substrate it increases the resistance of the substrate that limits the flow of current in the solution so after a certain period the growth of zinc oxide as well as flow of current reduces by a margin. So we can conclude that the in spite of constant potential due to semiconducting properties of ZnO, current as well as growth of ZnO get hampered by a margin with the passage of time. Now we will elaborate and explain the formation procedure utilizing the data that we had found during electrodeposition using our proposed set-up.

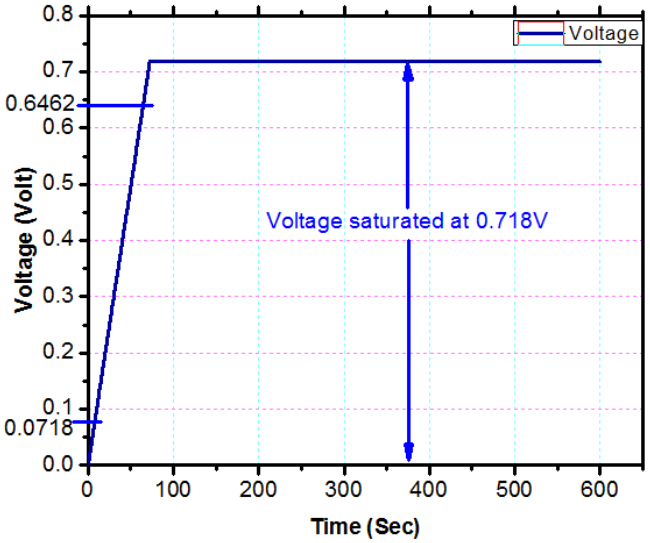

Fig. 4. Voltage versus Time curves.

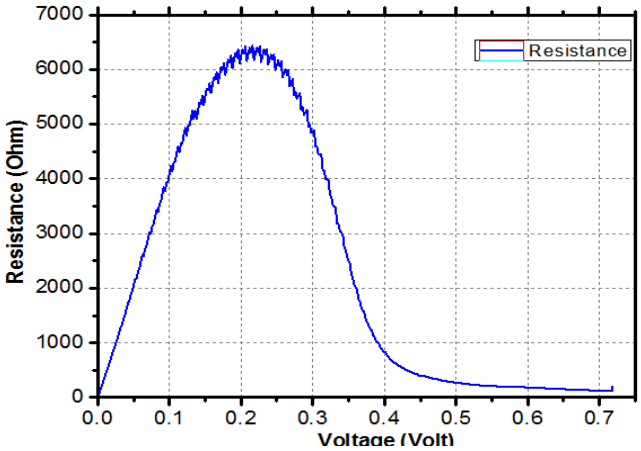

Fig. 5. Resistance versus Voltage curve

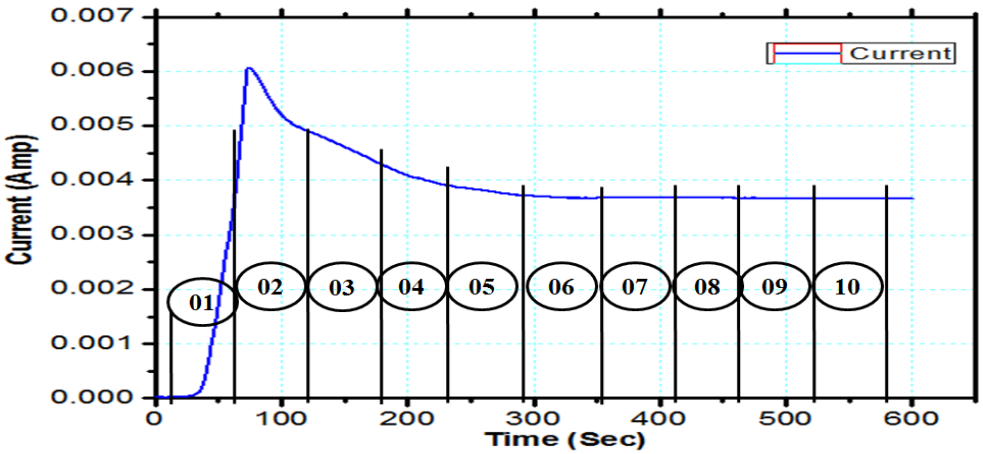

Fig. 6. Current versus Time curve
(the ten separate regions indicates ten speculated steps of deposition).

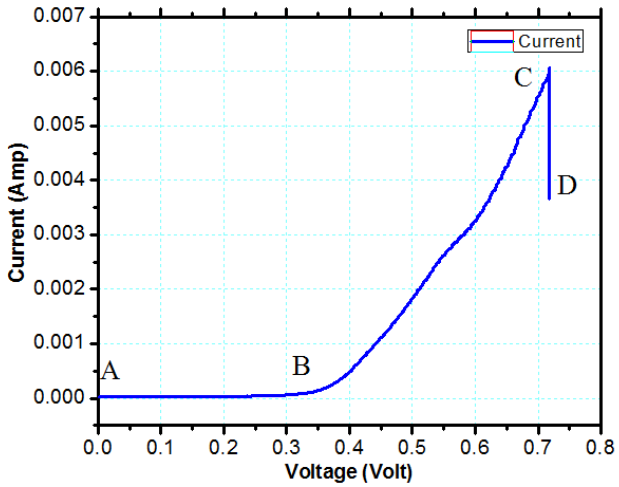

Fig. 7. Current vs Voltage curves

During the starting of rising time (fig. 4.), there exists lower affinity between the ions due to low potential (0.0712 V) between the electrodes that results higher resistance ultimately very lower current through the

circuit, in this period some Zn^{++} ions directly deposits on FTO as Zn and some $Zn(OH)^{+}$ on FTO to form ZnO adhesively, this happened because at initial state electrolyte lacks of OH^{-} to form $Zn(OH)^{+}$, so deposition rate on the electrode (cathode:-FTO) is very low (fig. 6: 0 to 50 seconds). Here one thing needs to be remember if all the deposited materials were purely conductive that is metal (Zn, conductivity of metal and FTO are very same), conductivity would be increased with the increase in the number of ions in the electrolyte, but thorough observation of fig. 5, fig. 6 and fig. 7. does not satisfy that possibility could be happened. In that case, current was crucially bounded by a straight line falling down slowly after achieving the rated voltage (CD portion in fig. 7.).

So with the increase in potential difference between electrodes more ions (NO_2^{-} & OH-) form in the electrolyte (according to equation 01), so current increases along with deposition rate. Increasing hydroxyl ions (OH^{-}) in the electrolyte affiliate the revealed Zn^{2+} to form $Zn(OH)^{+}$ consequently ZnO on FTO.

The rising time of voltage is 57.8 seconds (fig. 4, from 7.212 seconds to 65.012 seconds), we consider this interval as resolution and analyze the whole experiment depending upon the number of electrons flowed in between these one resolution each times. The whole time period of experiment divides into 10 separate steps, during first step (rising) (from 7.212 seconds to 65.012 seconds), second step (65.212 seconds to 122.411 sec), third step (122.612 sec to 180.012 seconds), fourth step (180.21 sec to 237.612 seconds), fifth step (237.812 sec to 295.212 sec), sixth step (295.212 sec to 352.411 sec), seventh step (352.611 sec to 410.012 sec), eighth step (410.212 sec to 467.411 sec), ninth step (467.612 sec to 524.812 sec), and tenth step (525.012 sec to 582.212 sec) consecutively the number of electrons that flew through the circuit are 5507, 29585, 25463, 22424, 21035, 20445, 20426, 20413, 20360 and 20338 (all data are calculated according fig. 6, utilizing MATLAB). In the first two steps number of electrons has been increased, but at rated voltage after achieving its apex the number of electrons in each step decreases exponentially (fig. 6.).

The above figures evolve a clear concept, that on to the FTO surface something deposits (ZnO-semiconductor) that hinders the flow of current through the circuit. Within 72.212 seconds indicated by the maximum current (fig. 6.), deposited composites (ZnO) cover the maximum surface of FTO causing the further flow of electrons limited through the circuit.

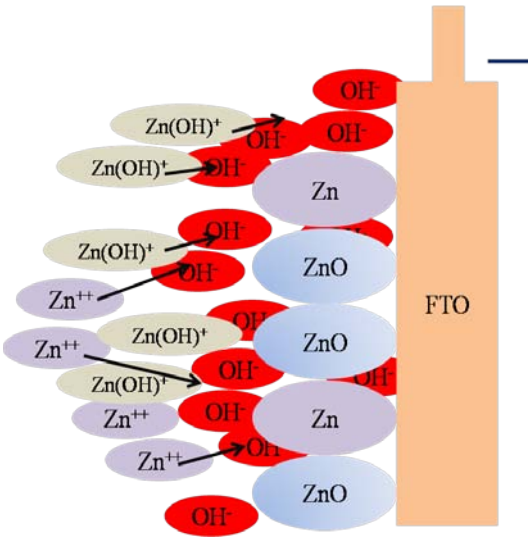

Fig. 8. Visualization of deposition in between middle of the second steps to the end

In between middle of second step and the last step current is exponentially reduced and saturated after a certain period, this phenomenon is depicted by the above figure (fig. 8.), after a thin deposition of ZnO and Zn(very little in amount) on FTO, it loses it metal like conductivity but tunnel like access made due to accumulation of zinc (Zn) on FTO causes further electron to flow resulting equation 1 to conduct, consequently more OH^{-} produces around cathode, meanwhile some more Zn ions (Zn^{++}) enhance the tunnel as before and repeat the system cyclically. OH^{-} in turn affiliate the dissolved Zn^{++} to form $Zn(OH)^{+}$ that stay in a queue to form more ZnO on FTO (fig. 8.).
We use a 25ml, 0.5M $Zn(NO_3)_2$ electrolyte in order to provide sufficient amount of NO_3^{-} to produce enough OH^{-} and NO_2^{-} by reduction of nitrogen. By conventional mathematics of chemistry, the electrolyte contains

some 1.50575×10^{22} nitrate ions (NO_3^-), which in turn easily enable to meet some 212387 (calculated from I-T data of LabVIEW; fig. 4.) electron that flows during 10 minutes of experiment in the purpose of producing OH^- causing reduction of Nitrogen.

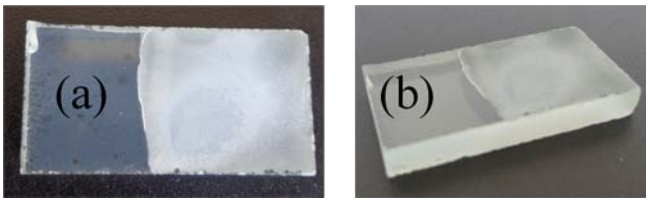

Fig. 9. Image of deposited material on FTO, (a) Top view, (b) 3D view

The above figure (fig. 9.) depicts the post condition of deposition. After drying in normal air we found a resistivity of 1.52MΩ along 1cm distance on the surface of deposited material. Similarly on the surface of FTO it was 0.00Ω in one centimeter distance.
As we use an electrolyte of dehydrated zinc nitrate and distilled water, so deposited material having current limiting as well as highly resistive property can only be an oxide type semiconductor composition (Zinc oxide).

5. Conclusion

We were successfully arranged the two electrodes electrodeposition set-up in a computerized controlled way, where all electrical quantities were visible as graphics and data were stored five times in a second as text at the target directory inside the computer without using any data logger as extra manual device. Finally using the mentioned set-up, we fabricated a film of ZnO on FTO successfully and explained its deposition mechanism that resembles with the inbuilt ZnO formation mechanism.

6. References

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