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 <u>Original Research Article</u>

 2
 EFFECT OF TEMPERATURE ON THE IRON SULPHUR RATIO OF

 3
 PYRITE DEPOSITED BY AEROSOL ASSISTED CHEMICAL VAPOUR

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 DEPOSITION METHOD

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Abstract: Pyrite semiconducting film was deposited on a glass substrate from a single source
precursor (FeS₂CN(Et)₂)₃) using aerosol assisted chemical vapour deposition AACVD. The
p-XRD pattern of the deposited films shows that pure pyrite was deposited at 300°C whereas
mixture of pyrite and marcasite was deposited at 350°C, 400°C and 450°C. EDX analysis
shows that semiconducting pyrite was deposited at 300°C whereas metallic pyrite
was deposited at 400°C and 450°C.

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15 Keyword: EDX, XRD, semiconducting pyrite, metallic pyrite, AACVD.

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17 **1. INTRODUCTION**

Iron pyrite (cubic FeS2) is a promising photovoltaic (PV) material and has some properties 18 that makes it suitable for photovoltaic application, these solid state properties include, 19 indirect band gap of 0.98eV, optical absorption coefficient of 10^{5} cm⁻¹ (for $\lambda < 900$ nm), 20 21 adequate minority carrier diffusion length of (100-1000) nm, essentially infinite elemental abundance, high photocurrent and high quantum efficiencies ¹⁻⁶. Pyrite solar cell has some 22 advantages over other photovoltaic materials such as cheap, nontoxic and could make a 23 significant impact even with lower efficiencies, because most of the materials reported as 24 photovoltaic use either toxic or not very abundant elements such as cadmium, lead or indium, 25 etc^7 which means that these materials cannot contribute significantly to a future energy 26 supply. Recent estimates of the annual electricity potential as well as material extraction costs 27 and environmental friendliness led to the identification of materials that could be used in 28 photovoltaic applications on a large scale⁸ The most promising materials include iron and 29 copper sulfides. Various methods have been used to deposit pyrite, such as, flash 30 evaporation⁹, metal organic chemical vapour deposition¹, vacuum thermal evaporation¹⁰, ion 31 beam and reactive sputtering¹¹, chemical vapour deposition¹², electrodeposition¹³ and molecular beam deposition¹⁴. Other methods include chemical spray pyrolysis¹⁵, vapour 32 33 transport¹⁶, hot injection method¹⁷, sulphurization of iron oxides¹⁸, and plasma assisted 34 sulphurization of iron¹⁹. Each technique of thin film deposition has its own advantages and 35 disadvantages. Herein, we used solution based method, precisely Aerosol Assisted Chemical 36 Vapour Deposition (AACVD) method to deposit nanocrystals of pyrite from a solution using 37 single source precursor that is Diethyldithiocarbamato iron (III) $(FeS_2CN(Et)_2)_3)$ and 38 39 characterized the deposited films using XRD and EDX to determine the structure and ironsulphur ratio of the deposited films. We have previously reported optical properties of pyrite 40 deposited by AACVD from Diethyldithiocarbamato iron (III) and in this research work, we 41 reported the effect of depositing temperature on iron-sulphur ratio. 42

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44 **2. EXPERIMENTAL**

All reagents were used as purchased and solvents were distilled prior to use. All syntheses
were performed under an inert atmosphere of dry nitrogen using standard schlenk techniques.
Elemental analysis was performed by the University of Manchester micro-analytical
laboratory. Mass spectra were recorded on a Kratos concept 1S instrument. Infra-red spectra
were recorded on a Specac single reflectance ATR instrument (4000-400 cm⁻¹, resolution 4

50 cm⁻¹). Melting points were recorded on a Barloworld SMP10 Melting Point Apparatus. p-51 XRD studies were performed on an Xpert diffractometer using Cu-K α radiation. The samples 52 were mounted flat and scanned between 20° and 70° with a step size of 0.05° and various 53 count rates. Films were carbon coated using an Edward's E306A coating system before 54 carrying out EDX analysis. EDX was carried out using a DX4 instrument.

55 **2.1 Precursor synthesis**

The precursor, Diethyldithiocarbamato iron (III) was prepared as described previously by Paul O'Brien group and Nair *et al* 2001 20,21,22

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59 2.2. Preparation of solution

The solution was prepared by dissolving 0.3g (0.6 mmol) of the precursor (FeS₂CN(Et)₂)₃) in 15ml of toluene in a two-necked 100ml round bottom flask and concentration of 0.04mol/dm³ was achieved. The substrates used were glass microscope slides. The glass slides were cut to size approximately 1 x 2 cm² by hand. The substrates were not handled with bare fingers rather with hand gloves to avoid contamination. The substrates were cleaned with detergent solutions, rinsed with distilled water and then rinsed with acetone, methanol and distilled water and finally dried before use.

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68 2.3. Deposition of thin films of Pyrite by AACVD

15ml of the solution was poured into the two-necked round bottom flask with a gas inlet that 69 allowed argon (carrier gas) to pass into the solution to aid the transport of the aerosol. A piece 70 of reinforced tubing was used to connect the flask to the reactor tube. Platon flow gauge was 71 used to control argon flow rate. Seven glass substrates (approximately $1 \times 2 \text{ cm}^2$) were placed 72 73 inside the reactor tube which is placed in a Carbolite furnace maintained at a certain 74 temperature. The precursor solution in a two-necked round bottom flask was kept in a water 75 bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No 1077). 76 The solution was evaporated and the generated aerosol droplets of the precursor were transferred into the hot wall zone of the reactor by the carrier gas. This precursor vapour 77 78 reached the heated substrate surface where thermally induced reactions and film deposition 79 took place at 60mins and a particular temperature. The temperature of the Carbolite furnace was varied in step of 50°C starting from 300°C to 450°C. The time was kept at 60mins, the 80 81 flow rate kept at 160sccm and the concentration kept at 0.04mol/dm3 throughout the experiment. The experiment was repeated a good number of times, **Table 1** summarized the 82 parameter that was varied during the deposition. 83

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S/N	Slide	Argon	Concentration	Time of	Temperature	Repeated
	No	flow rate	of precursor	deposition	of deposition	times
		(sccm)	(mol/dm ³)	(minutes)	(°C)	
1	E	160.00	0.04	60.00	300.00	3
2	F	160.00	0.04	60.00	350.00	3
3	G	160.00	0.04	60.00	400.00	3

4	Н	160.00	0.04	60.00	450.00	3
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88 Table 1 Variation of temperature at 60 minutes and 0.04mol/dm³

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3. RESULTS AND DISCUSSION

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The **p-XRD** patterns of the deposited films are shown in **figure 1**. From **Figure 1**, the vertical 92 line represents the standard cubic pyrite (FeS_{1.96} (ICDD No. 01-073-8127)). The film 93 deposited at 300°C (slide E) corresponds to pure polycrystalline pyrite with no trace of 94 marcasite peak, whereas the films deposited at 350°C (slide F), 400°C (slide G) and 450°C 95 (slide H) show mixture of polycrystalline pyrite and marcasite. The marcasitic peak increases 96 as the deposition temperature increases. The peaks at 26.3°, 39.2°, 52.1° (20) correspond to 97 marcasitic peak (ICDD No. 04-003-2016). The preferred orientation of the films deposited, 98 99 both pure and impure pyrite, lies on (111), (200), (210), (211), (220), (311) and (032) planes of reflection. 100



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102 Figure 1. p-XRD patterns of deposited films, at 300°C (slide E) pure polycrystalline pyrite (FeS_{1.96} 103 (ICDD No. 01- 073-8127) is formed with planes of reflection on (111), (200), (210), (211), (220), 104 (311) and (023), at 350°C (slide F), 400°C (slide G), 450°C (slide H) mixture of pyrite and marcasite 105 (+) (ICDD No. 04-003-2016) is formed.

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4.3 EDX OF MY FILMS 107

108 The EDX analysis of all the films shows the presence of Iron and Sulphur Figure 2. Quantification of iron and sulphur in the films shows that ratio of iron and sulphur increases 109 with temperature. The Iron:Sulphur ratio is approximately 50:50 at 300°C and 350°C, 60:40 110 at 400°C and 64:36 at 450°C (Table 2). This result shows that the deposited semiconducting 111

- 112 film changes from semiconducting to metallic film at high temperature. The observed sulphur
- deficiency at elevated temperature is attributed to the fact that sulphur evaporates from thin
- 114 films at high temperatures 23,24 .





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117 Figure 2 EDX spectrums of the deposited films

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Deposition time		Temperature						
(minutes)	300°C		350°C		400°C		450°C	
	Fe %	S %	Fe %	S %	Fe %	S %	Fe %	S %
60	48	52	50	50	60	40	70	30

Table 2 The iron:sulphur ratio for the films deposited at 300°C, 350°C, 400°C and 450°C.

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121 **4. CONCLUSION**

122 Semiconducting pyrite was successfully deposited on glass substrate from a single source 123 precursor (FeS₂CN(Et)₂)₃) using AACVD. The p-XRD patterns of the deposited films show that polycrystalline pure pyrite is formed at 300°C whereas at 350°C, 400°C and 450°C 124 polycrystalline mixture of pyrite and marcasite is formed. We also observed that the 125 temperature of the glass substrate has significant effect on the iron:sulphur ratio of the 126 deposited films. The iron:sulphur ratio of 48:52, 50:50, 60:40 and 70:30 were obtained at 127 300°C, 350°C, 400°C and 450°C respectively. This shows that at high deposition temperature, 128 semiconducting pyrite film becomes metallic pyrite film. These results show that iron 129 sulphide minerals are typified by a range of significant temperature induced composition and 130 131 phase transformation.

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