IR Photoresponse and Electrically Assisted Transition in VO₂ Thin Films Prepared by Single-Step Chemical Vapor Deposition

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Experimental details



Figure 1. Structure of Vanadyl acetylacetonate

The polycrystalline VO_2 thin films studied in this work were synthesized by a horizontal hot wall, low pressure Chemical Vapor Deposition (CVD). The schematic of CVD for the synthesis

of vanadium oxides [1,2] is reported elsewhere. Volatile metal organic precursor, Vanadium acetyl acetonate precursor was taken in an aluminium boat in the vaporizer. The deposition chamber was made of quartz which can be heated resistively to 1000 °C. High purity Argon gas carried the precursor vapors to the reaction zone whereas high purity oxygen gas acts like an oxidant (reactant gas) and was sent through a different line. The cleaned substrates were kept in the furnace and heated to a temperature of ~ 520 °C.

Precursors Preparation

MOCVD requires the use of a subliming precursor. We use a metal-organic precursor called Vanadylacetylacetonate (VO(acac)₂). The structure of VO(acac)₂ is shown in Fig.1

Synthesis procedure for Vanadylacetylacetonate Precursors

The complex was synthesized using the procedure adopted in the lab already. Vanadium pentoxide from SD Fine chemicals, AR grade of 5.00 g was added to a mixture of 10 ml of conc. H₂SO₄ (sulphuric acid) in 10 ml distilled water and 24 ml of ethanol. After the reaction mixture was refluxed for about 1.5 hours, it was cooled. To the cooled mixture, 12ml of the ligand (acetylacetone from Aldrich chemicals 99%) was added. This mixture was neutralized by adding a solution of 40 g of anhydrous Na₂CO₃ (sodium bicarbonate)in 300 ml of distilled water, while it was stirred using a magnetic stirrer. The resulting mixture was cooled in ice water for 15 min and subsequently filtered. The resulting dark green product was washed with ice-cold water and dried using a suction pump. VO(acac)₂ prepared in this way was purified by recrystallizing it in dichloromethane.

IR Confirmation of VO (acac)₂

The characterization of the complex was already reported[1]. The FTIR confirmation was recorded on a JASCO 410FT-IR spectrometer, with the complex KBr in the range 4000-400 cm⁻¹. The observed peaks were matched with the standard data available in the literature . All the expected peaks are observed, confirming the formation of the complex. Figure 2. Shows the FTIR spectrum of VO(acac)₂.

Assignments	Bonds
(Wavenumber	
cm ⁻¹)	
2998	Sp ³ CH
1557,1528	acac C-C and C-
	0
1357	CH ₃
1287,1189	C-0
1018,997	С-Н
798,610	V-O

Table.1 IR frequencies and their assignment



Figure 2. FTIR spectra of VO(acac)2

Thin films of Vanadium Oxide (VO₂) was grown in a hot-wall, horizontal, low-pressure MOCVD system built in house. The deposition chamber was maintained at 520 °C. Cleaned substrates were mounted on a stainless steel substrate holder, sloped at \sim 15 ° with respect to the horizontal, placed at the centre of the deposition chamber. Argon was purged as carrier gas at a flow rate of 100 SCCM. High-purity oxygen was carried through a separate gas line as the reactive gas with a flow rate of 50 SCCM. Depositions of the films were carried out for 15 min.

The total pressure in the reactor was maintained at 19.2 Torr by a capacitance manometer (MKS). About 0.1 g of the precursor, taken on an aluminum boat was placed inside the vaporizer. The precursor was kept in the vaporizer at a temperature of 185 °C. The system was evacuated to the base pressure through the purge-line. The furnace, gas lines and vaporizer were heated to their respective (chosen) temperatures, purging the system with high purity. When all the temperatures were stabilized, the purging with argon gas was stopped and the flow of carrier gas (argon) and the reactant gas (oxygen) was adjusted to the desired values using the MFCs. The valve separating the deposition chamber and vaporizer was then opened initiating film deposition. The total pressure of the system was monitored; the controls were adjusted in order to maintain a constant pressure. After the deposition conditions are tabulated in Table.2.

Parameters	Value
Furnaca tamparatura	520°C-
runace temperature	550°C
Deposition Time	15 min
Oxygen flow rate	50 SCCM
A	100
Argon now rate	SCCM
Vaporizer temperature	185°C
Pressure	19.2 Torr

Table2: Depos	sition conditions u	sed in CVD on	Si substrates
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X-ray diffraction Analysis

Fig.3 shows the X-ray diffraction pattern of VO(acac)₂. The XRD pattern of the complex matches with the reported pattern (JCPDS file 23-1965) for VO(acac)₂. It crystallizes in triclinic system belonging to the space group P-1.



Figure 3. XRD of VO(acac)₂

Thermogravimetric (TGA) analysis

Thermal analysis of the precursor was carried out at atmospheric pressure using a TA Instruments SDT Q600 simultaneous DTA/TGA system with a dual beam horizontal setup from room temperature to 500 °C. Crystalline VO(acac)₂ was crushed well before loading. About 10 mg of this precursor was taken in a platinum crucible (90 μ l). Alumina was used as the reference. The experiments were carried out in the flow of ultra-high purity N₂ gas[1].

TGA measurements of VO(acac)₂ were carried out at ambient pressure at a heating rate of 10 ° C/min. Fig.4 shows the TGA plot of VO(acac)₂. It shows a single-step weight loss starting at 130° C and saturating around 300 ° C. Below 175 °C, the precursor shows clean sublimation, indicating that it can be useful as a CVD precursor.



Figure 4. TGA curve of VO(acac)₂

Chemical Vapor Deposition of VO2



Figure 5. Schematic of CVD

The schematic of the MOCVD set up is shown in Figure 5. Thin films of Vanadium Oxide (VO_2) were grown in a hot-wall, horizontal, low-pressure MOCVD system built in house. The deposition chamber is made of fused quartz that can be heated resistively up to 1000 °C. Cleaned substrate was mounted on a stainless steel substrate holder, sloped at ~15 ° with respect to the horizontal, placed at the centre of the deposition chamber. The slope gives an improved uniformity of film thickness over the substrate area. Chromel-Alumel thermocouple was inserted in a hole kept in the substrate holder to measure the growth temperature. One end of the deposition chamber was connected to the gas flow system and the other was connected to a rotary vacuum pump through a flexible bellow, used for achieving the desired low pressure. The assembly of needle valve and throttle valve connected at the vacuum pump allowed precise control of pressure during deposition.

The finely powdered precursor was placed in an aluminum boat inside a cylindrical vaporizer made of stainless steel, heated resistively. The temperature was regulated by a PID temperature controller. High-purity argon (Ar) gas was used as carrying gas for precursor transport. A supplementary gas line also carrying Ar was used to purge the deposition chamber. High-purity oxygen was carried through a separate gas line and was used as the reactant gas. Electronic mass flow controllers (MFCs) were used to precisely control the gas flow during deposition. Valves capable of withstanding temperatures upto 315 °C, placed at different nodes of the gas lines were used to restrict and regulate the gas flow. Heating tapes wound on the gas line between the vaporizer and the deposition zones were used to heat the line to avoid precursor condensation on

the inner walls of the gas lines. Programmable temperature controllers were used in order to maintain the temperature of the deposition chamber, precursor vaporizer and gas-handling lines accurately. The total pressure in the reactor was precisely measured by a capacitance manometer (MKS)

XPS of O1s Spectra



Figure 6. Deconvoluted O 1s XPS spectra of the VO₂ thin films deposited at 520 ° C In the O1s spectra, 531.6 eV and the splitting is attributed to the presence of SiO₂ or other hydoxyl groups. From the V 2p and O 1s spectra it is understood binding energy (BE) for V⁴⁺ and O 1s increases with substrate temperature.

Piezoforce Microscopy Measurements: PFM measurements were carried out on VO2 samples deposited on Stainless steel substrates.



Figure 7. Force-deflection Curve



Figure 8. Tip Bias Vs Amplitude



Figure 9. Phase image (a) 0 ° scan (b) 90 ° scan. The boundaries are shifted 90 ° with respect to the 0 ° scan.

Stability of VO2 thin films

The thin films exhibited the same response properties after several times and cycles of measurements thus proving the stability of the films for longer periods of time even after 1 year of synthesis. The temperature variable experiments were performed from 25 °C to 115 °C in 5 °C intervals and each time allowing the set temperature to equilibrate for 5 minutes before the measurement was carried out. Fig. 10. shows the additional set of current-voltage data performed on the same thin film to show that the film is of high quality and that the film is stable. Normalized resistance as a function of temperature.



Fig. 10 Normalized resistance against temperature plot taken on the same film at different times.

Reference:

[1] U. Ail, "Thin Film Semiconducting Metal Oxides By Nebulized Spray Pyrolysis And MOCVD, For Gas-Sensing Applications," Materials Research Centre, Indian Institute of Science, 2008

[2] M.B. Sahana, "Metalorganic Chemical Vapour Deposition of Thin Films of Vanadium Oxides: Microstructure and Properties," Materials Research Centre, Indian Institute of Science, 2003.