Deposition of Vanadium Oxide Thin Films- A Review

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Abstract

Vanadium oxides are of novel interest for the last few decades due to their interesting electrical, structural and optical properties. The characteristic features of vanadium oxide films can be altered by doping, stress, annealing, and strain. It is also observed that characteristics of the vanadium oxide thin films depends upon various deposition conditions such as nature of substrate, gas pressure, temperature of substrate and deposition time. Therefore, it becomes an interesting area to explore the changes in the properties of vanadium oxide films grown by different techniques. In this review, we survey the fabrication techniques of VO_2, V_2O_5 and V_6O_{13} thin films; namely by RF sputtering, reactive rf sputtering, pulsed laser deposition, sol-gel method, e-beam evaporation, and spin coating method.

Keywords Thin Films, Vanadium Oxide, Sputtering, Fabrication

1. Introduction

Transition metal oxides show fascinating properties such as metal to insulator transition (MIT), magneto-resistive effect and high temperature superconductivity due to the vacant d-orbitals of transition metals. Among the transition metal oxides, vanadium oxides are one of the most interesting systems that have been studied by researchers. Vanadium oxygen system has many oxides, like VO, VO_2, V_2O_5, V_2O_3, V_6O_{13}, and V_4O_9 and due to the multiple oxidation states (+2 to +5) of vanadium species (Peys et al. 2013). These oxides draw notable attention due to highly useful metal-insulator transition (MIT) along with a sudden modification in electrical, optical and structural properties of the material. These changes make them interesting materials for various applications such as gas sensors, lithium-ion batteries, electric and optical switching devices, electro-chromic devices, and smart windows etc. (Zhou et al. 2013; Batista et al. 2011; Zou et al. 2017). This first order MIT and electro-chromic behavior of vanadium oxide thin films have been well-studied over the last fifty years but the mechanism behind this intriguing phenomenon is not properly well understood. Metal to insulator transition in transition metal oxides was firstly pointed (Morin 1959) in titanium and vanadium lower oxides. These oxides behave like metals and appeared to show MIT at a particular temperature. This transition in titanium and vanadium oxides can be described by partially filled d-bands. It was given that

these partially filled bands split into upper band which is empty and a set of lower occupied bands. Lower bands have an antiferromagnetic spin alignment and are localized. This metal-insulating transition was further explained by the cation-cation interaction in metal oxides (Goodenough 1960). It was observed that the interactions between octahedral-site cations were responsible for cation-cation interaction. This interaction was classified as strong and weak depending upon the separations of cations. Later, Alder and Brooks (1967) explained this transition by two theoretical models. According to first model, transition was due to the antiferromagnetic exchange interaction and it was found that it gives a second order transition by solving the parameters of the model. In second model, it results from the lattice distortion and gives a first order transition. It was found that stoichiometry of vanadium oxide thin films varies with deposition techniques and process parameters, such as oxygen concentration, substrate temperature, thickness of the film, nature of substrate and nature of target material. Different techniques like RF sputtering, pulsed laser deposition (PLD), e-beam evaporation, sol-gel deposition and thermal evaporation method were used by the researchers to grow the vanadium oxide thin films on different substrates.

In this review different techniques along with deposition parameters used for the synthesis of vanadium oxide thin films are discussed in detail.

2. Deposition of Vanadium Dioxide (VO_2) thin films

Vanadium dioxide (VO_2) is an amazing oxide and attracted much attention as it shows MIT above the room temperature (Morin 1959; Alder & Brooks 1967). The transition temperature of VO_2 film is 341 K. Structural, electrical and optical (IR region) properties of vanadium dioxide dramatically changes at this temperature. Thin film (thickness ~1200 Å) of VO_2 was deposited by DC and RF reactive sputtering by using vanadium (V) solid target on glass substrate (Duchene et al. 1972). Deposition parameters were: RF power 50 W, pressure $2\text{-}3\times10^{-3}$ Torr, peak voltage 2-3 kV, and oxygen percentage vary from 0% to 20%. Shift in the transition temperature was observed along with change in optical refractive index in comparison to vanadium dioxide crystal. Stoichiometry effect on the VO_2 films was studied by Griffiths & Eastward (1974). Films were fabricated from metallic V target on fused quartz, sapphire and carbon coated sapphire by rf sputtering in the oxygen argon atmosphere. Deposition parameters had been optimized, total gas pressure 7.5 mTorr, rf power 350W, deposition rate 35A°/min. It was observed that unit cell volume increased due to the change in oxygen concentration in the film. Vanadium vacancies or interstitial defects changed the oxygen concentration in the film. It

was also observed that resistivity and MIT can be controlled by electrons concentration. Thin films of vanadium oxide were deposited on fused silica from metallic V target by rf magnetron sputtering. The conditions of deposition were; pressure during sputtering 1Pa, target substrate distance 60 mm, RF power 120 W, substrate temperatures 400-480°C (Wang et al. 2001). Micro Raman results showed that annealed film consists of three (3) regions, black region (V_6O_{13}), yellow region (VO_2) and white amorphous region. Effect of microstructure and orientation of the films on the MIT temperature was studied by Lappalainen et al. (2008) Films were grown on the sapphire and magnesium oxide substrates by PLD experiment. Fabrication parameters were as follow: temperature of substrate 400°C, pulse duration 25ns, pulse energy density 3J/cm^2, pulse repetition rate 5Hz and V_2O_5 pellet as target material, It was shown that significant variation in the properties might be due to the internal stress of the film. A stress free film showed largest change in the MIT and optical properties.

Effect of strain on the electrical properties was also studied by Kikuzuki and Lippmaa (2010). Films were deposited on TiO_2 substrate from V_2O_3 target by PLD method. KrF ablation laser of wavelength 248nm operated at 1Hz, substrate temperatures are 440°C and 480°C, fluence 0.6J/cm^2 and oxygen pressure 4.4 mTorr. It was observed that effect of strain on resistance appeared to be nearly two times larger than purely thermal change. Hall and magneto resistance measurements (Ruzmetov et al. 2009) were studied in the thin film of VO_2 at 12 Tesla DC magnetic fields. Thin films of VO_2 (~ 100nm thick) were fabricated on silicon substrate from V target by reactive rf sputtering at 550°C substrate temperature. Base pressure in the chamber was 2×10^{-8} Torr and oxygen (8.8%) + Argon (91.2%). Experimental results showed that resistivity of the films dropped over third orders of magnitude at MIT and the resistance increased by the application of magnetic field in semiconducting region. All the observed changes were due to the change in electron density from 10^{19} to 10^{23} cm^{-3} at the MIT.

Thin films of thermochromic VO_2 were fabricated by rf cathodic sputtering by using V target on silica (Guinneton et al. 2004). Films were deposited in the mixture Ar/O_2 environment, oxygen concentration varies between 0.5 to 2%, chamber pressure 5 to 30 mTorr and substrate temperature was 380°C. Role of thickness on optical properties of films were studied and it was found that optical contrast is related to the film density and low particle size. Vanadium dioxide thin films (~200 nm) were fabricated on silicon substrate from VO_2 target by magnetron sputtering. Growth temperature and gas flow were kept at 550°C and (97.9 + 2.1) SCCM for Ar plus O_2. Polycrystalline (011) direction oriented films were obtained (Yang et al. 2011).

Doping affects the properties of vanadium oxide thin films, optical properties of VO_2 doped films deposited on Si and Ge by spin coating method were studied by Beteille & Livage (1998). Films were deposited from solution of $VO(OAm^t)_3$ in isopropanol Pr^iOH. Electrical properties of Al^{3+} doped films deposited on Si and glass by PLD were studied by Chen et al. (2009). For deposition, a pulsed KrF excimer laser (wavelength 248 nm), with pulse duration 25 ns, laser fluence 2-3 J/cm^2, repetition rate fixed at 50 Hz and vanadium pentoxide target was used for laser ablation. Percentage of Al^{3+} was varied by changing ablation time on Al_2O_3 target. It was found that with 10% Al^{3+} doping, the transition temperature dropped and narrowed the hysteresis loop. Effect of doping with high valence cations (W, Mo, Nb) on vanadium dioxide thin films was studied by Batista et al. (2011). Films were fabricated by direct current magnetron sputtering from V target on SiO_2 coated glass. Processing conditions used for the fabrication of films were working pressure 4×10^{-3}mbar, oxygen/argon ratio 14.3%, DC current 0.5A, substrate temperature 450°C, and deposition time 5 min. It was observed that W doping effectively altered the properties of the films in comparison to Mo and Nb.

Properties of vanadium dioxide can be tuned by the stress relaxation mechanism. Vanadium oxide films were fabricated by rf sputtering on Si substrate and hafnium oxide layer sandwiched between them and also on the top side of film. Deposition conditions were; V_2O_5 target, substrate temperature set as 550°C, RF gun power 125 W, Gas mixture of 98.75 SCCM Ar and 1.25 SCCM O_2, total pressure maintained at 10 m Torr. Results revealed that value of transition temperature decrease to 45°C when vanadium oxide film was confined between hafnium oxide layers in comparison to bottom hafnium oxide layer to 59°C (Viswanath et al. 2011). VO_2 thin films were fabricated from VO_2 target by reactive sputtering (argon and oxygen mixture environment) on different substrates (Cui & Ramanathan 2011). The sputtering was performed at 10 mTorr pressure, substrate temperature 550°C, deposition time 3h, and rf source power set at 150 W. Thickness of films was nearly 300 nm. Films deposited on TiO_2 were more stable than Al_2O_3 and MgF_2 substrate. Higher stability of the films deposited on TiO_2 substrate was due to lattice matching near the interface. Yang et al. (2010) deposited vanadium dioxide films on two different sapphire (c-cut and r-cut) substrates by PLD method. Films were deposited by using KrF laser, with pulse width 25ns, oxygen pressure 10 mTorr, repetition rate 10 Hz, and substrate temperature used on c-sapphire and r-sapphire was 600 and 500°C respectively. It was observed that single orientation film was obtained on c-cut sapphire whereas double orientation film

deposited on r-cut sapphire. It was also found that strain in the r-cut sapphire reduced the transition temperature of film. VO_2 thin films were deposited on c-Al_2O_3 and Si substrates from V target by PLD and sputtering method. Deposition parameters for PLD were KrF Laser with fluence of 3J/cm2, Substrate temperature was 773K, oxygen gas at 2.66Pa and repetition rate of laser 10Hz. A phase between monoclinic and tetragonal (intermediate phase) appeared in the films deposited on Al_2O_3 substrate and no such phase was deposited in case of Si substrate. It was analyzed that Intermediate phase was due to the strained structure of films deposited on Al_2O_3 (Okimura et al. 2010). Effect of oxygen concentration from 1% to 7% was reported on the VOx films deposied by reactive rf sputtering from vanadium target (Lee et al. 2007). Films were deposited at the deposition conditions, rf power 100 W and working pressure 0.67 Pa. The base pressure of the growth chamber was $1.33–2.67\times10^{-4}$ Pa. Deposition rate of the films depends upon the oxygen concentration, films at 2% O_2 concentration were mainly contain VO_2 phase. Gupta et al. (2011) were deposited VO_2 thin films by PLD technique on Si substrate. KrF laser with pulse duration of 25 ns, pulse rate 5 Hz, pulse energy density 2-3 J/cm^2, and substrate temperature 500°C was used for the fabrication of films. They reported the high energy ions irradiation effect on the transition characteristics of VO_2. It was observed that localized defects change the transition characteristics from first order to second order.

Vanadium dioxide thin films were obtained from the reduction of V_2O_5 target. Samples were deposited on Si substrate from reactive RF sputtering at 450°C and 550°C. Experimental conditions for deposition of films were, Rf power 50 W, deposition time 15, 30 and 45 mins, and distance between electrode is 50 mm. Oxygen gas pressure was kept low in comparison to argon gas flow (Saitzek et al. 2008). No change in optical properties was observed above film thickness 100-120 nm. VO_x films were deposited by reactive RF sputtering by metallic vanadium (V) target on Si substrate in argon and Ar plus oxygen atmosphere (Zhang et al. 2016). Deposition parameters were substrate temperature 500°C, power 200W, deposition time 120 min, total gas pressure 1.33kPa and O_2 flow rate varies from 1.3 to 3 SCCM. Various stoichiometry films were obtained from oxidation and reduction of the films by annealing. Raman characterization results revealed that different phase evoluation took place. Thickness of the deposited film also affects the structural and MIT temperature characteristics. Vanadium dioxide thin films of were fabricated on glass substrate by magnetron sputtering. Base pressure was 2×10^{-3} Pa, substrate temperature 100°C, and the O_2/Ar flow ratio (O_2/Ar = 1/98) was constant0. Results revealed that MIT temperature depended upon grain size and multi structured film was obtained in the thinner

films (Luo et al. 2014). Annealing also alter the properties of the films, Wu et al. (2008) reported the annealing effect on vanadium oxide films. Thermal evaporation method was used to deposit the films from V_2O_5 target on quartz substrate. Films were deposited at room temperature and other deposition conditions were; distance between source and substrate was 30 cm, deposition pressure 5.0×10^{-3} Pa, and electrical current was 120 A. As-deposited films were annealed at 300°C and then cooled down to room temperature. It was reported that post annealing converted the amorphous film into crystalline V_2O_5 and a small amount of VO_2.

3. Deposition of vanadium pentoxide (V_2O_5) thin films

V_2O_5 phase in vanadium oxygen system is the most stable oxide. It exists in single crystal structure and has the topmost oxidation state (+5) in vanadium oxygen system. It is an n-type semiconducting material with band gap of nearly 2.0 eV and shows metal insulator transition at 530 K. Pure V_2O_5 powder was used to deposit the films of vanadium pentoxide by laser ablation method. The laser used for experiment was Nd:YAG with power density 10^8 W, repetition rate of 10 Hz, pulse width 10 ns, oxygen partial pressure 50-300 mTorr, and substrate temperature was nearly 300°C. The deposition of vanadium pentoxide (V_2O_5) films on different substrate and temperature (Julien et al. 1999) exhibited that films fabricated on the glass were amorphous or polycrystalline while those on the silicon highly crystalline in nature. Effect of biasing on the optical properties of vanadium oxide thin films was studied by (Krishna and Bhattacharya 1997). Films were deposited on glass substrate from solid V target by DC magnetron sputtering technique. Films were deposited in the Ar/O_2 mixture with ar pressure 3-6 mTorr and oxygen pressure was 0.5 to 1.5 mTorr. Discharge current varies from 0.375 to 0.5 A, bias voltage varied from o to -150V, and distance between substrate and target is 5 cm. It was found that refractive index of the film increased with negative bias voltage. Films were transformed from amorphous to crystalline phase at -75 V bias voltage. V_2O_5 films (~1 μm) were prepared by sol gel method on glass and silicon. Vanadium pentoxide powder was heated at 900°C in a crucible for 1 hr in air and then quenched the molten oxide into room temperature. The obtained solution is placed on substrate and excess solvent was evaporated. Colour of the film changed to dark red from brownish yellow by cathodic polarization. This electro chromic behavior was explained by movement of hydrogen atoms inside the film. It was also observed that increased water content change the electrical and optical properties of the film (Pergament et al. 2002).

Films of V_2O_5 were deposited on heated glass by spray pyrolysis technique at 250°C and 400°C (Kaid 2006). Aqueous solution of ammonium meta-vanadate of concentration 0.1 to 0.5M is

used for the deposition of films. Films deposited at 250°C were amorphous in nature, while those deposited at 400°C showed crystalline in nature. It was shown that deposition temperature affects the optical properties and structural (Kumar et al. 2008) of V_2O_5 thin films. Vanadium pentoxide powder target was used to deposited vanadium oxide thin films on amorphous glass substrate by evaporation technique. Pressure of the deposition chamber is 10^{-4} Pa, distance between target and source is 7 cm, and deposition rate 0.25 μm/min. It was shown that films deposited at room temperature were homogenous and uniform but amorphous in nature. Films deposited above 200°C were crystalline in nature and colour of the films changed from yellow to dark brown. Kumar et al. (2003) deposited the vanadium oxide thin films for the application in bolometer. Films were deposited on glass by PLD method from V_2O_5 target by using a Nd:YAG laser pulses. Fabrication conditions were; pulse width 8 ns, pulse energy 50 mJ, substrate temperature 300K and repetition rate 10 Hz. It was observed that 1.4 J/cm^2 was the most favorable fluence of the laser for the fabrication of high quality films used in detector applications. Vanadium pentoxide (V_2O_5) nano particle films (Luo et al. 2010) were deposited by reactive DC sputtering onto glass and KBr substrate from vanadium target varying substrate temperature from 433K to 593K. Basic deposition parameters were initial pressure of the chamber 2×10^{-3} Pa and deposition time 30 min. Microstructure of the films and infrared absorption were changed with increase in substrate temperature. Other properties like electronic activation energy, optical transmittance decrease because of the change in microstructure of the films.

Optical properties of V_2O_5 coating were studied by Esther et al. 2015 and it was observed that optical band gap increases as the thickness of film decreases. Pure V_2O_5 target was used as a target material for the fabrication of films by RF magnetron sputtering on quartz and Si substrate. The deposition was performed at RF power 700 W, working pressure set at 5×10^{-6} mbar, thickness of films also affects the structural properties of vanadium oxide thin films and was studied by Park et al. (2002). Films were grown on Pt coated Si substrate from V target by RF sputtering at 200°C substrate temperature. Films were grown in the deposition parameters as, target to substrate distance 5 cm, rf power and the total pressure during deposition were 200 W and 10 mTorr respectively and films were deposited in a mixed environment (Ar/O_2), ratio of Ar/O_2 was 80/20. It showed that if the thickness of the film was less than 800 nm, V_6O_{13} phase appeared and at higher thickness V_2O_5 phase was formed with orientation perpendicular to the substrate.

Effect of substrate on vanadium pentoxide films was studied and found that films deposited on alumina, silicon and quartz were polycrystalline in nature while on glass amorphous exhibit (Bhat et al. 2015). Films were deposited on the different substrate from inorganic V_2O_5 powder and hydrogen peroxide by spin coating technique. Variation in the properties (thickness, phase purity and structure) of films (deposited on different substrate) was due to the adhesive force between substrate and film. Vanadium oxide films were deposited on glass and silicon by hot-filament technique and effect of annealing at different temperature was studied (Scarminio et al. 2017). Films were grown in a stainless-steel chamber in the oxygen environment maintained at a pressure of 0.24 Pa. A vanadium filament (42 mm long and diameter 1 mm) was heated by 22 Ampere AC power supply. Films are formed by thermal reactions between vanadium and oxygen in the HFMOD at the filament surface. Characterization results revealed that as-deposited film has amorphous nature and when annealed at 200°C and 300°C film becomes opaque but still amorphous in nature. Annealing at 500°C, a polycrystalline V_2O_5 phase in orthorhombic structure with optical band gap 2.25 eV was obtained.

Effect of Ag doping was studied on thin films of vanadium oxide deposited on glass and silicon. Films were fabricated by two laser ablation plasmas from highly pure (99.99%) vanadium and silver target. Laser beam was divided in two beams by using a beam splitter, Nd:YAG laser was used with pulse duration 10 ns, fluence 8.2 J/cm^2 and vanadium and silver targets were used as material sources. It was found that photocatalytic properties of the films were improved by incorporation of Ag. As concentration of Ag increased, coexistence of different phases of vanadium oxides appeared and structure of the film also changed from crystalline V_2O_5 to acicular containing Ag (Gonzalez-Zavala et al. 2018). Gupta et al. (2020) were used rf sputtering and pulsed laser deposition techniques for the fabrication of vanadium oxide thin films. Films were grown on silicon substrate from V_2O_5 powder pellet. Deposition parameters of rf sputtering were: RF power 120 W, working pressure 2.2×10^{-2} mbar and substrate temperature 300°C. For PLD method, deposition conditions were; substrate kept at 500°C, KrF laser (λ= 248nm), pulse duration of 25 ns, fluence 2 J/cm^2, O_2 pressure 6 mTorr, fabrication time 20 min and pulse rate 10Hz. A mixed phase (VO_2 and V_2O_5) was obtained by both the techniques.

4. Deposition of Hexavanadium Tredecaoxide (V_6O_{13}) thin films

Vanadium pentoxide (V_2O_5) and hexavanadium tredecaoxide **(**V_6O_{13}) are close to VO_2 in stoichiometry. V_6O_{13} is a mixed valance compound with two V^{4+} cations for every V^{5+} cation with monoclinic structure as V_2O_5. V_6O_{13} thin films of variable thickness (90 nm, 170 nm and

200 nm) were deposited on p-type silicon wafer (Rua et al. 2009) by pulsed laser deposition technique from metallic vanadium pellet. The films were fabricated in argon and oxygen atmosphere at a total pressure of 70 mTorr (10 to 15 SCCM pressure for oxygen), pressure in chamber 10^{-6} Torr, KrF excimer laser (λ= 248 nm), fluence 4J/cm^2, pulse duration 20 ns and substrate temperature 500°C. By controlling the oxidation state, V_6O_{13} films were deposited by the aqueous procedure on SiO_2 and Al_2O_3 substrate (Peys et al. 2013). A crystalline V_6O_{13} phase was formed by annealing the samples at 500°C for 30 minutes in 0.1% O_2 environment.

Effect of deposition temperature on the vanadium oxide thin films was studied by Sahana & Shivashankar (2004). Films were deposited from vanadyl acetylacetonate by chemical vapor deposition method on quartz substrate. Films were grown in the temperature range from 550 to 610 °C for 2 hours. Total chamber pressure was 100 Torr and oxygen flow rate was high (350 SCCM) compared to that of argon (60 SCCM). It was found that films deposited below 560°C, mixed phase of V_2O_5, V_6O_{13} and V_4O_9 obtained and above 560°C to 580°C it alternated between V_2O_5 and V_6O_{13}. Phase transformation occurred at higher temperature is explained on the basis of similarity in structure of V_2O_5 and V_6O_{13}. Multiple phase transition observed when vanadium oxide films were heated from room temperature to 550°C (Begara et al. 2017). Films were grown from vanadium target on silicon and Al_2O_3 by e-beam evaporation method. Deposition parameters were, substrate temperature 500°C, deposition rate 0.05 nm/s and oxygen pressure 8×10^{-2} Pa. As-deposited films are annealed at 550°C in oxygen atmosphere for 15 min. Results showed that as the temperature increase, film undergoes multiple phase transition, i.e. V_3O_7,VO2, V_2O_5, and V_6O_{13} along with change in electrical conductivity. This may be due to the absorption of oxygen at higher temperature and at 550°C stable V_2O_5 phase was obtained. V_6O_{13} films were deposited by thermal decomposition process at different temperatures on Si substrate. V_6O_{13} films were deposited from powdered V_6O_{13} prepared by thermal decomposition of NH_4VO_3. This powder was placed on substrate and placed in a furnace. The furnace temperature was set at 150°C for 2 hrs then increases to 400°C for next 4 hrs and then 550°C maintained for one hour. It was observed that growth conditions affect the electro chromic nature of the film. Films deposited at higher temperature delivered low diffusion coefficient while films deposited at room temperature showed higher and constant diffusion coefficient (Gorenstein et al. 1995). Effect of post annealing and irradiation of swift heavy ions was studied by (Gupta et al. 2019, 2022) on rf sputtered thin films of vanadium oxide. Films were grown by sputtering in Ar/O

environment (99.25 SCCM Ar and 0.75 SCCM O_2). Total working pressure 2.0×10^{-2} mbar, substrate temperature 500°C, RF power 120 W, and deposition time 1.5 hrs. It was observed that the V_6O_{13} phase was formed by rf sputtering, this phase was transformed into V_6O_{13}, VO_2, and V_2O_5 a mixed phase by post-annealing. Irradiation changed the (003) plane of V_6O_{13} to (012) plane of V_2O_3 phase.

5. Conclusion

Vanadium oxide thin films draw attention of researchers due to fascinating properties and applications in different areas. There are different fabrication techniques used by researchers to deposit thin films of vanadium oxide. It was always a challenging task to grow a single phase vanadium oxide thin film. RF sputtering and pulsed laser deposition (PLD) techniques are mostly used by researches to grow thin films of vanadium oxide. Solid vanadium target is frequently used as a source material. It is reported that properties of vanadium oxide thin films varies with process parameters, such as oxygen concentration, substrate temperature, thickness of the film, nature of substrate and nature of target material. Oxygen concentration is a pivot factor during deposition of vanadium films because of the multiple oxidation state of vanadium (V). Summarizing the above mentioned data, we can state that enhancement in deposition techniques and development of novel synthesis approaches are very perspective in order to obtain good quality of vanadium oxide thin films.

6. References

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