Niobium Oxides

Subjects: Surfaces, Coatings & Films
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Definition

Niobium oxides (NbO, NbO₂, Nb₂O₅), being a versatile material has achieved tremendous popularity to be used in a number of applications because of its outstanding electrical, mechanical, chemical, and magnetic properties. Nb₂O₅ films possess a direct band gap within the ranges of 3.2–4.0 eV, with these films having utility in different applications which include; optical systems, stainless steel, ceramics, solar cells, electrochromic devices, capacitor dielectrics, catalysts, sensors, and architectural requirements. With the purpose of fulfilling the requirements of a vast variety of the named applications, thin films having comprehensive properties span described by film composition, morphology, structural properties, and thickness are needed.

1. Introduction

Niobium, a chemical substance having a symbol of Nb, is a ductile transition metal which is light grey in colour with a crystalline structure [1]. Niobium, also known as columbium and titanium in their pure states, possesses similar hardness [2] as well as a ductility comparable to that of iron. Niobium can often be discovered in pyrochlore and columbite minerals, resulting in its previous name of “columbium”. The oxidation of niobium in the earth’s atmosphere is extremely slow, thus its utilization in jewellery as a hypoallergenic substitute to nickel [3]. Niobium alongside its oxides are crucial and strategically high materials of technology. Niobium oxides bring about several diverse and remarkable properties, ranging from its solid appearance in nature, to its, melting point of 1512 °C, its insolubility in water but solubility in hydrogen fluorides (HF), its density and molecular weight of 4.47 g/cm³ and 265.81. All these to a large extent, make it a flexible group of material. Precisely, niobium oxides have shown enormous potentials in numerous applications of technology which include, transparent conductive oxides, solid electrolytic capacitors, photochromic devices, dye-sensitized solar cells and memristors.

2. Characteristics of Niobium Oxides

Niobium oxides which are n-type semiconductors are inclusive of, but not limited to; niobium dioxide (niobium (IV) oxide) NbO₂, niobium monoxide (niobium (II) oxide) NbO, niobium pentoxide (niobium (V) oxide) Nb₂O₅, as there are other different oxides of the metal. Each of these oxides of niobium have distinct electrical characteristics which ranges from metallic conducting NbO to semiconducting NbO₂ with κ (kappa) value of 3.9 [4], and then insulating Nb₂O₅ [5], which thermodynamically, is the most stable oxide, with the smallest available energy formation [6][7]. However, the existence of NbO and NbO₂ in a film, would influence the general properties of the Nb₂O₅ films [8]. Niobium pentoxide (Nb₂O₅) is consistently formed when sufficient oxygen is supplied during the reaction process. Nevertheless, when other oxides of niobium are required, there should be a limitation to the quantity of oxygen supplied to avoid the production of Nb₂O₅. The difficulty here is in discovering the appropriate amount of oxygen flow rate needed to attain the needed stoichiometry [9].

A study, which was performed by Venkataraj et al. [10], stated that an oxygen flow rate beyond 7 sccm was adequate for the formation of the pentoxide film, though no report was made on the fabrication of the other oxide films. However, the system of niobium–oxygen is remarkably a complicated one, because very little deviations in the precise stoichiometry of Nb₂O₅ greatly influences the material's physical properties. For example, with little deficiency in oxygen, the Nb₂O₅ transits from insulating to n-type semiconducting properties [11].

The finding of electrochromism by Reichman and Bard from Nb₂O₅ in the year 1980 [12], resulted in the oxide being comprehensively researched after being discovered as an encouraging electrochromic material for its application in devices due to its exceptional chemical stability as well as corrosive resistivity in both acid and base forms. This electrochromism is an occurrence in relation to a continuous and reversible optical change generated electrochemically, of which its macroscopic effect is a colour change [13]. Thin films of niobium oxide exhibit transparent to brownish, grey or blue electrochromism with the introduction of ions like Li⁺ or H⁺, and this alters the optical transmittance to 24% from an initial 78% (l ¼ 600 nm) with a colouring or bleaching kinetic of about 10 s. However, the standard of an electrochromic material is measured based on its coloration efficiency, which is its contrast in transmittance between the
coloured or bleached states as a result of the injected charge, the time of response, and the chemical stability. Consequently, these features are contingent on the Nb$_2$O$_5$ film’s material characteristics. One of the advantages of Nb$_2$O$_5$ films over tungsten oxide is this ability of it being able to obtain various colours ranging between brown amorphous layers to blue crystalline layers. Therefore, based on its crystalline nature, the transparent Nb$_2$O$_5$ thin film in its reduced state shows distinct colours of blue, brown or grey.

The similarities between the properties of microscopic and macroscopic materials, as well as their deposition variables, provides very essential guidance and direction towards the optimization of materials for different applications. This particularly, is typical of oxides of niobium, as films of niobium oxides display varying electrical and optical features as a result of their deposition techniques and production parameters. Niobium oxide films have been suggested to be used in a vast array of technical applications, which include, sensing materials, assisting with the process of catalysis, and for use as biocompatible coatings. Niobium (V) oxide (Nb$_2$O$_5$) which possesses a high dielectric constant and a high refractive index of 200 and 2.4 respectively, with also a broad band gap of 3.2–4.0 eV, can be employed in many different applications like; electrochromic devices, capacitor dielectrics, oxygen sensors, solar cells and catalysts. Niobium pentoxide which is a transparent dielectric material is a perfect material for use in the development of capacitors, and in the application of optical systems. As a result of its higher permittivity in contrast to that of Ta$_2$O$_5$, it has been proposed as a logical alternative for Ta$_2$O$_5$ in the application of capacitors of solid electrolyte tantalum/tantalum pentoxide ($\text{Ta}_2\text{O}_5$) films, in which the dielectric layer of the oxide is produced via a porous metal powder compressed by anodic oxidation. This is because, not only does it have comparable anodization characteristics to Ta$_2$O$_5$ but also offers the benefit of more abundance in the nature, thus the reduction in price of raw materials. Also, a comprehensive study has been performed on the pentoxide, labelling it as gate dielectrics in complementary metal oxide semiconductors (CMOS) components which as well displays exceptional catalytic qualities. High-κ (kappa) Nb$_2$O$_5$ can be used as a substitute to the traditional gate dielectric of SiO$_2$, so as to satisfy the requirements for miniaturization of the dynamic random-access memory along with the complementary metal oxide semiconductor components. The composition of the Nb$_2$O$_5$ films is literally affected by the partial pressure of oxygen and the deposition temperature which may probably lead to an alternation in the dielectric constant. Latest reports have included the incorporation of Nb$_2$O$_5$ in electrode materials of electrochemical applications, and this has brought about outstanding performance which is largely attributed to the intercalation pseudo-capacitance effect of the doped Li$^+$. Niobium monoxide which is a metallic material has a superconductivity at 1.38 K, thus, is being utilized in superconducting circuits as a resistor. Niobium dioxide itself is a semiconductor which has exceptional field-switching qualities, and has proved itself as an encouraging assistance for platinum in the oxidation of methanol as well as a reducing agent in fuel cell technologies. Niobium dioxide experiences a transition from metal to insulator with drastic transformations in resistivity and magnetic sensitivity, as well as a concurrent structural transformation to a rutile structure from a rutile twisted structure. NbO$_2$’s transition characteristics have so much similarity with those of Vanadium dioxide (VQ). However, NbO$_2$’s transition temperature is far greater than VO$_2$’s, (approximately 340 K), making it less vulnerable to Joule heating and thus more attractive in circuit applications. It is stated that the metal insulator transition (MIT) in NbO$_2$ could also be activated by an applied electrical field, thus making it appealing for use as a switching material which can possibly be utilized as nanoelectronic devices. Regardless of the NbO$_2$’s desirable features, experimental works on NbO$_2$ thin films have been minimal as a result of the challenges faced in the production of NbO$_2$ films of high quality. Its production is difficult since Nb$^{4+}$ does not exist as a stable niobium oxidation state and thus is easily over-oxidized. Previous works indicated that amorphous and polycrystalline films of NbO$_2$ were formed by sputtering an NbO$_2$ material from the reduction of Nb$_2$O$_5$ through the chemical vapour transport method.

Due to its high electrical properties, niobium oxide has been employed as a dopant for a number of materials such as tin, vanadium, lead, tungsten, titanium, bismuth and zinc. However, one problem with niobium oxide is its complex crystal system which consists of a wide variation of polymorphic forms, even though these polymorphic forms bring about interesting successions with regards to structural phases. These phases are usually determined by the NbO$_6$ octahedral groups, which form different arrangements from the rectangular block of columns. The most frequently identified phases were termed H, M, T, B and TT, with their occurrences resting on the techniques and conditions used in preparation. For example, the most thermodynamically stable is the H-phase, and it is the one produced at temperatures beyond 1000 °C. The other phases of T and TT acquire stability at temperatures ranging
between 650–800 °C and 300–550 °C respectively. Nb$_2$O$_5$ has a wide range of features, based on their crystalline modifications. The H-phase has a high dielectric constant of approximately 100 [58], the T-phase is highly electrochemically stable with an outstanding cycling performance [67], while the electrochromic devices are especially interested in the TT-phase.

Many different effective deposition procedures have been implemented for the production of the thin films of Nb$_2$O$_5$, which consists of, sol gel process [58], chemical spray pyrolysis [16], sputtering [14], pulsed laser deposition [18], biased target ion beam deposition [49], electron beam evaporation [59], electrochemical deposition process [56], chemical vapour deposition (CVD) [17] and atomic layer deposition (ALD) [61].

References


Keywords
Niobium Oxides, Niobium, Nb; Semiconductors; Electrochromism; Solar cells; Capacitors

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