

Niobium Oxides

Subjects: [Materials Science](#), [Coatings & Films](#)

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Niobium oxides (NbO , NbO_2 , Nb_2O_5), 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. Nb_xO_y 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.

Niobium Oxides, Niobium, Nb

Semiconductors

Electrochromism

Solar cells

Capacitors

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) NbO_2 , niobium monoxide (niobium (II) oxide) NbO , niobium pentoxide (niobium (V) oxide) Nb_2O_5 , 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 NbO_2 with κ (kappa) value of 3.9 ^[4], and then insulating Nb_2O_5 ^[5], which thermodynamically, is the most stable oxide, with the smallest available energy formation ^{[6][7]}. However, the existence of NbO and NbO_2 in a film, would influence the general properties of the Nb_2O_5 films ^[8]. Niobium pentoxide (Nb_2O_5) 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 Nb_2O_5 . 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 Nb_2O_5 greatly influences the material's physical properties. For example, with little deficiency in oxygen, the Nb_2O_5 transits from insulating to n-type semiconducting properties [11].

The finding of electrochromism by Reichman and Bard from Nb_2O_5 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 $\frac{1}{4}$ 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_2O_5 film's material characteristics. [14]. One of the advantages of Nb_2O_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 [15]. Therefore, based on its crystalline nature, the transparent Nb_2O_5 thin film in its reduced state shows distinct colours of blue, brown or grey [16].

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 [17]. Niobium oxide films have been suggested to be used in a vast array of technical applications, which include, sensing materials [18][19][20], assisting with the process of catalysis [21][22][23], and for use as biocompatible coatings [24][25][26]. Niobium (V) oxide (Nb_2O_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 [27][28][29]. 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 [30]. As a result of its higher permittivity in contrast to that of Ta_2O_5 , it has been proposed as a logical alternative for Ta_2O_5 in the application of capacitors of solid electrolyte tantalum/tantalum pentoxide (Ta_2O_5) [31], 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_2O_5 but also offers the benefit of more abundance in the nature, thus the reduction in price of raw materials [32][33][34]. Also, a comprehensive study has been performed on the pentoxide, labelling it as gate dielectrics in complementary metal

oxide semiconductors (CMOS) components [35] which as well displays exceptional catalytic qualities. High- κ (κ) Nb_2O_5 can be used as a substitute to the traditional gate dielectric of SiO_2 [3][9], so as to satisfy the requirements for miniaturization of the dynamic random-access memory along with the complementary metal oxide semiconductor components [36][37]. The composition of the Nb_2O_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 [38]. Latest reports have included the incorporation of Nb_2O_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^+ [7][39][40]. Niobium monoxide which is a metallic material has a superconductivity at 1.38 K [41], thus, is being utilized in superconducting circuits as a resistor [42].

Niobium dioxide itself is a semiconductor which has exceptional field-switching qualities [43], 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 [44]. 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 [45]. NbO_2 's transition characteristics have so much similarity with those of Vanadium dioxide (VO_2) [46]. 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 [47][48], thus making it appealing for use as a switching material which can possibly be utilized as nanoelectronic devices [47]. 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 [49]. Previous works indicated that amorphous and polycrystalline films of NbO_2 were formed by sputtering an NbO_2 material from the reduction of Nb_2O_5 through the chemical vapour transport method [50].

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 [51], 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 [52], and it is the one produced at temperatures beyond 1000 °C. The other phases of T [53] and TT [54][55] acquire stability at temperatures ranging between 650–800 °C and 300–550 °C respectively. Nb_2O_5 has a wide range of features, based on their crystalline modifications. The H-phase has a high dielectric constant of approximately 100 [56], the T-phase is highly electrochemically stable with an outstanding cycling performance [57], 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_2O_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 [\[60\]](#), chemical vapour deposition (CVD) [\[17\]](#) and atomic layer deposition (ALD) [\[61\]](#).

References

1. Meija, J.; Coplen, T.B.; Berglund, M.; Brand, W.A.; De Bièvre, P.; Gröning, M.; Holden, N.E.; Irrgeher, J.; Loss, R.D.; Walczyk, T.; et al. Atomic weights of the elements 2013 (IUPAC Technical Report). *Pure Appl. Chem.* 2016, 88, 265–291.
2. Samsonov, G.V. Mechanical Properties of the Elements. In *Handbook of the Physicochemical Properties of the Elements*; Springer Science and Business Media: Berlin/Heidelberg, Germany, 1968; pp. 387–446.
3. Knapp, B. *Elements of Geographical Hydrology*; Unwin Hyman Limited: London, UK, 2002.
4. Zhao, Y.; Zhang, Z.; Lin, Y. Optical and dielectric properties of a nanostructured NbO₂ thin film prepared by thermal oxidation. *J. Phys. D: Appl. Phys.* 2004, 37, 3392–3395.
5. Tanabe, K. Catalytic application of niobium compounds. *Catal. Today* 2003, 78, 65–77.
6. Jacob, K.T.; Shekhar, C.; Vinay, M.; Waseda, Y. Thermodynamic Properties of Niobium Oxides. *J. Chem. Eng. Data* 2010, 55, 4854–4863.
7. Venkataraj, S.; Drese, R.; Liesch, C.; Kappertz, O.; Jayavel, R.; Wuttig, M. Temperature stability of sputtered niobium–oxide films. *J. Appl. Phys.* 2002, 91, 4863–4871.
8. Bach, D.; Stormer, H.; Schneider, R.; Gerthsen, D.; Sigle, W. EELS Investigations of Reference Niobium Oxides and Anodically Grown Niobium Oxide Layers. *Microsc. Microanal.* 2007, 13.
9. Foroughi-Abari, A.; Cadien, K.C. Growth, structure and properties of sputtered niobium oxide thin films. *Thin Solid Films* 2011, 519, 3068–3073.
10. Venkataraj, S.; Drese, R.; Kappertz, O.; Jayavel, R.; Wuttig, M. Characterization of Niobium Oxide Films Prepared by Reactive DC Magnetron Sputtering. *Phys. Status Solidi* 2001, 188, 1047–1058.
11. Ou, J.Z.; Rani, R.A.; Ham, M.-H.; Field, M.R.; Zhang, Y.; Zheng, H.; Reece, P.; Zhuiykov, S.; Sriram, S.; Bhaskaran, M.; et al. Elevated Temperature Anodized Nb₂O₅: A Photoanode Material with Exceptionally Large Photoconversion Efficiencies. *ACS Nano* 2012, 6, 4045–4053.
12. Reichman, B.; Bard, A.J. Electrochromism at Niobium Pentoxide Electrodes in Aqueous and Acetonitrile Solutions. *J. Electrochem. Soc.* 1980, 127, 241–242.
13. Granqvist, C. Inorganic Non-Oxide Electrochromic Materials. In *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, The Netherlands, 1995; pp. 421–430.

14. Cabanel, R.; Chaussy, J.; Mazuer, J.; Delabouglise, G.; Joubert, J.C.; Barral, G.; Montella, C. Electrochromism of Nb₂O₅ Thin Films Obtained by Oxidation of Magnetron-Sputtered NbNx. *J. Electrochem. Soc.* 1990, 137, 1444–1451.
15. Schmitt, M.; Aegerter, M. Electrochromic properties of pure and doped Nb₂O₅ coatings and devices. *Electrochimica Acta* 2001, 46, 2105–2111.
16. Mujawar, S.; Inamdar, A.; Patil, P.; Patil, P. Electrochromic properties of spray-deposited niobium oxide thin films. *Solid State Ionics* 2006, 177, 3333–3338.
17. Granqvist, C. Electrochromism and smart window design. *Solid State Ionics* 1992, 53, 479–489.
18. E Gimon-Kinsel, M.; Balkus, J.K.J. Pulsed laser deposition of mesoporous niobium oxide thin films and application as chemical sensors. *Microporous Mesoporous Mater.* 1999, 28, 113–123.
19. Rho, S.; Jahng, D.; Lim, J.H.; Choi, J.; Chang, J.H.; Lee, S.C.; Kim, K.J. Electrochemical DNA biosensors based on thin gold films sputtered on capacitive nanoporous niobium oxide. *Biosens. Bioelectron.* 2008, 23, 852–856.
20. Ficarro, S.B.; Parikh, J.R.; Blank, N.C.; Marto, J.A. Niobium(V) Oxide (Nb₂O₅): Application to Phosphoproteomics. *Anal. Chem.* 2008, 80, 4606–4613.
21. Tamai, T.; Haneda, M.; Fujitani, T.; Hamada, H. Promotive effect of Nb₂O₅ on the catalytic activity of Ir/SiO₂ for NO reduction with CO under oxygen-rich conditions. *Catal. Commun.* 2007, 8, 885–888.
22. Cvelbar, U.; Mozetič, M. Behaviour of oxygen atoms near the surface of nanostructured Nb₂O₅. *J. Phys. D: Appl. Phys.* 2007, 40, 2300–2303.
23. Prado, A.G.; Bolzon, L.B.; Pedroso, C.P.; Moura, A.O.; Costa, L.L. Nb₂O₅ as efficient and recyclable photocatalyst for indigo carmine degradation. *Appl. Catal. B Environ.* 2008, 82, 219–224.
24. Eisenbarth, E.; Velten, D.; Breme, J. Biomimetic implant coatings. *Biomol. Eng.* 2007, 24, 27–32.
25. Starikov, V.V.; Starikova, S.L.; Mamalis, A.G.; Lavrynenko, S.N.; Ramsden, J.J. The application of niobium and tantalum oxides for implant surface passivation. *J. Biol. Phys. Chem.* 2007, 7, 65–68.
26. Tanvir, M.T.; Aoki, Y.; Habazaki, H. Improved electrical properties of silicon-incorporated anodic niobium oxide formed on porous Nb–Si substrate. *Appl. Surf. Sci.* 2009, 255, 8383–8389.
27. Le Viet, A.; Reddy, M.V.; Jose, R.; Chowdari, B.V.R.; Ramakrishna, S. Nanostructured Nb₂O₅ Polymorphs by Electrospinning for Rechargeable Lithium Batteries. *J. Phys. Chem. C* 2010, 114, 664–671.
28. Blanquart, T.; Niinistö, J.; Heikkilä, M.; Sajavaara, T.; Kukli, K.; Puukilainen, E.; Xu, C.; Hunks, W.; Ritala, M.; Leskelä, M. Evaluation and Comparison of Novel Precursors for Atomic Layer

- Deposition of Nb₂O₅ Thin Films. *Chem. Mater.* 2012, 24, 975–980.
29. Zhou, X.; Li, Z.; Wang, Y.; Sheng, X.; Zhang, Z. Photoluminescence of amorphous niobium oxide films synthesized by solid-state reaction. *Thin Solid Films* 2008, 516, 4213–4216.
 30. Lai, F.; Lin, L.; Huang, Z.; Gai, R.; Qu, Y. Effect of thickness on the structure, morphology and optical properties of sputter deposited Nb₂O₅ films. *Appl. Surf. Sci.* 2006, 253, 1801–1805.
 31. Störmer, H.; Weber, A.; Fischer, V.; Ivers-Tiffée, E.; Gerthsen, D. Anodically formed oxide films on niobium: Microstructural and electrical properties. *J. Eur. Ceram. Soc.* 2009, 29, 1743–1753.
 32. Yoon, J.S.; Cho, S.W.; Kim, Y.S.; Kim, B.I. The production of niobium powder and electric properties of niobium capacitors. *Met. Mater. Int.* 2009, 15, 405–408.
 33. Choi, J.; Lim, J.H.; Lee, J.; Kim, K.J. Porous niobium oxide films prepared by anodization–annealing–anodization. *Nanotechnology* 2007, 18, 055603.
 34. Matylitskaya, V.A.; Bock, W.; Kolbesen, B.O. Nitridation of niobium oxide films by rapid thermal processing. *Anal. Bioanal. Chem.* 2008, 390, 1507–1515.
 35. Kukli, K.; Ritala, M.; Leskelä, M. Development of Dielectric Properties of Niobium Oxide, Tantalum Oxide, and Aluminum Oxide Based Nanolayered Materials. *J. Electrochem. Soc.* 2001, 148, F35–F41.
 36. Bharti, D.C.; Rhee, S.-W. Dielectric properties and X-ray photoelectron spectroscopic studies of niobium oxide thin films prepared by direct liquid injection chemical vapor deposition method. *Thin Solid Films* 2013, 548, 195–201.
 37. Cho, K.; Lee, J.; Lim, J.-S.; Lim, H.; Lee, J.; Park, S.; Yoo, C.-Y.; Kim, S.-T.; Chung, U.-I.; Moon, J.-T. Low temperature crystallized Ta₂O₅/Nb₂O₅ bi-layers integrated into RIR capacitor for 60 nm generation and beyond. *Microelectron. Eng.* 2005, 80, 317–320.
 38. Naito, K.; Matsui, T. Review on phase equilibria and defect structures in the niobium-oxygen system. *Solid State Ionics* 1984, 12, 125–134.
 39. Augustyn, V.; Come, J.; Lowe, M.A.; Kim, J.W.; Taberna, P.-L.; Tolbert, S.H.; Abruña, H.D.; Simon, P.; Dunn, B. High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat. Mater.* 2013, 12, 518–522.
 40. Tamang, R.; Varghese, B.; Mhaisalkar, S.; Tok, E.S.; Sow, C.H. Probing the photoresponse of individual Nb₂O₅ nanowires with global and localized laser beam irradiation. *Nanotechnol.* 2011, 22, 115202.
 41. Hulm, J.K.; Jones, C.K.; Hein, R.A.; Gibson, J.W. Superconductivity in the TiO and NbO systems. *J. Low Temp. Phys.* 1972, 7, 291–307.

42. Lo, W.; A Cardwell, D.; Bradley, A.D.; Doyle, R.; Shi, Y.; Lloyd, S. Development of non-weak link bulk YBCO grain boundaries for high magnetic field engineering applications. *IEEE Trans. Appl. Supercond.* 1999, 9, 2042–2045.
43. Shin, S.H.; Halpern, T.; Raccach, P.M. High-speed high-current field switching of NbO₂. *J. Appl. Phys.* 1977, 48, 3150.
44. Sasaki, K.; Adzic, R.R. Monolayer-level Ru-and NbO₂-supported platinum electrocatalysts for methanol oxidation. *J. Electrochem. Soc.* 2008, 155, B180–B186.
45. Bolzan, A.A.; Fong, C.; Kennedy, B.J.; Howard, C.J. A Powder Neutron Diffraction Study of Semiconducting and Metallic Niobium Dioxide. *J. Solid State Chem.* 1994, 113, 9–14.
46. Eyert, V. The metal-insulator transition of NbO₂: An embedded Peierls instability. *EPL Europhysics Lett.* 2002, 58, 851–856.
47. Kim, S.; Park, J.; Woo, J.; Cho, C.; Lee, W.; Shin, J.; Choi, G.; Park, S.; Lee, D.; Lee, B.H.; et al. Threshold-switching characteristics of a nanothin-NbO₂-layer-based Pt/NbO₂/Pt stack for use in cross-point-type resistive memories. *Microelectron. Eng.* 2013, 107, 33–36.
48. Pickett, M.D.; Williams, R.S. Sub-100 fJ and sub-nanosecond thermally driven threshold switching in niobium oxide crosspoint nanodevices. *Nanotechnol* 2012, 23, 215202.
49. Wang, Y.; Comes, R.B.; Kittiwatanakul, S.; Wolf, S.A.; Lu, J. Epitaxial niobium dioxide thin films by reactive-biased target ion beam deposition. *J. Vac. Sci. Technol. A* 2015, 33, 21516.
50. Lee, S.-H.; Yoon, H.-N.; Yoon, I.; Kim, B.-S. Single Crystalline NbO₂ Nanowire Synthesis by Chemical Vapor Transport Method. *Bull. Korean Chem. Soc.* 2012, 33, 839–842.
51. Ramírez, G.; Rodil, S.; Muhl, S.; Turcio-Ortega, D.; Olaya, J.; Rivera, M.; Camps, E.; Escobar-Alarcón, L. Amorphous niobium oxide thin films. *J. Non-Crystalline Solids* 2010, 356, 2714–2721.
52. Kato, K. Structure refinement of H-Nb₂O₅. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1976, 32, 764–767.
53. Kato, K.; Tamura, S. Die Kristallstruktur von T-Nb₂O₅. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1975, 31, 673–677.
54. Holser, W.T. Compounds with the α -U₃O₈-type structure. *Acta Crystallogr.* 1956, 9, 196.
55. Ikeya, T.; Senna, M. Change in the structure of niobium pentoxide due to mechanical and thermal treatments. *J. Non-Crystalline Solids* 1988, 105, 243–250.
56. Cho, N.-H.; Kang, H.B.; Kim, Y.H. Dielectric characteristics and chemical structures of Nb₂O₅ thin films grown by sol-gel techniques. *Ferroelectrics* 1994, 152, 43–48.
57. Kumagai, N.; Tanno, K.; Nakajima, T.; Watanabe, N. Structural changes of Nb₂O₅ and V₂O₅ as rechargeable cathodes for lithium battery. *Electrochimica Acta* 1983, 28, 17–22.

58. Maček, M.; Orel, B. Electrochromism of sol–gel derived niobium oxide films. *Sol. Energy Mater. Sol. Cells* 1998, 54, 121–130.
59. Jelle, B.P. Electrochromic Smart Windows for Dynamic Daylight and Solar Energy Control in Buildings. *Electrochromic Mater. Devices* 2015, 419–502.
60. Zhitomirsky, I. Electrolytic deposition of niobium oxide films. *Mater. Lett.* 1998, 35, 188–193.
61. Huang, Y.; Xu, Y.; Ding, S.-J.; Lu, H.-L.; Sun, Q.-Q.; Zhang, D.W.; Chen, Z. Thermal stability of atomic-layer-deposited ultra-thin niobium oxide film on Si (100). *Appl. Surf. Sci.* 2011, 257, 7305–7309.

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