Indian Journal of Pure & Applied Physics
Vol. 59, December 2021, pp. 811-826

Advancement of High–k ZrO_2 for Potential Applications: A Review

Vishnu Chauhan[a,b], Deepika Gupta[a], Sonica Upadhyay[c], Jagjeevan Ram[d], Shalendra Kumar[e] & Rajesh Kumar[a]*

[a]University School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, New Delhi – 110 078, India

[b]Materials Science Group, Inter-University Accelerator Centre, New Delhi, 110 067, India

[c]Department of Computer Science & Engineering, Maharaja Surajmal Institute of Technology, New Delhi-110 058, India

[d]Department of Physics, Ramjas College, University of Delhi, Delhi, India

[e]Department of Physics, College of Science, King Faisal University, P.O. Box-400, Al-Ahsa 31982, Saudi Arabia

Received 13 September 2021; accepted 10 November 2021

Versatile zirconium oxide as a ceramic has propelled a rapid development of science and technology for diverse applications. Among the class of ceramics, it holds a distinctive position due to its excellent physical, chemical and mechanical properties owing to its phase transformation. Zirconia is high k- dielectric, mechanical resistance and high radiation tolerance material. Although, this material replaces SiO_2 due to its high dielectric constant so it can be employed to various memory device applications. It has essential implications in nuclear reactors, inert matrix fuel, nuclear waste systems, container for radioactive materials and designing of new materials owing to its high radiation tolerance property. Dentists proclaimed that zirconium oxide is “ceramic steel” where it has attracted prosthetic dentistry because of its strength and esthetics are admired. Addition of few percentages of stabilizers such as Y_2O_3, MgO and Ni *etc*. make it useful for specific applications. Zirconium oxide ceramic is indispensably used as an electrode and electrolyte in energy efficient solid state electrochemical devices (fuel cells) that generates electricity with good efficiency from natural gas and fuel cell plants and provides auxiliary power in vehicles. One of its important phase transformation mechanisms is being focused and extensively reviewed due to the effect of temperature variation and ion beam irradiation effect. The objective of current review is to present the knowledge of extensive properties, synthesis techniques and its various implications and guidelines for optical, medical, fuel cells, biological and electrical and memory devices and nuclear applications. The advantages of zirconia with respect to other oxide materials are also reviewed.

Keywords: High–k ZrO_2, Physical and chemical properties, Fule Cells, Opto-Electronic Devices Memory devices.

1 Introduction

The continuous demand of ceramic materials with extensive properties is necessary for enormous growth of science and technology. The potential properties of ceramics such as high temperature strength and chemical inertness in corrosive environments represent them as a promising class of materials[1]. Recently, many ceramic materials are being studied, for instance Al_2O_3, TiO_2, SiO_2, BeO, CeO_2, ZrO_2, HfO_2, Y_2O_3, MgO_2 and SnO_2 *etc*.[2,3]. Ceramics have led to wide range of applications in aerospace, energy & environment, capacitors and medical technology[4-6] as shown in Fig. 1. Among these ceramic materials, ZrO_2 is one of the unique ceramic widely used for technological and industrial applications. The incorporation of Al−Mg−Ga−Sn in zirconium oxide makes alloys as anode for alkaline aluminum batteries[7]. Usually, zirconia ceramics are used in laser mirrors, ionic conductors and refractory materials in furnaces. Zirconia exists in three temperature dependent polycrystalline phase i.e. monoclinic,

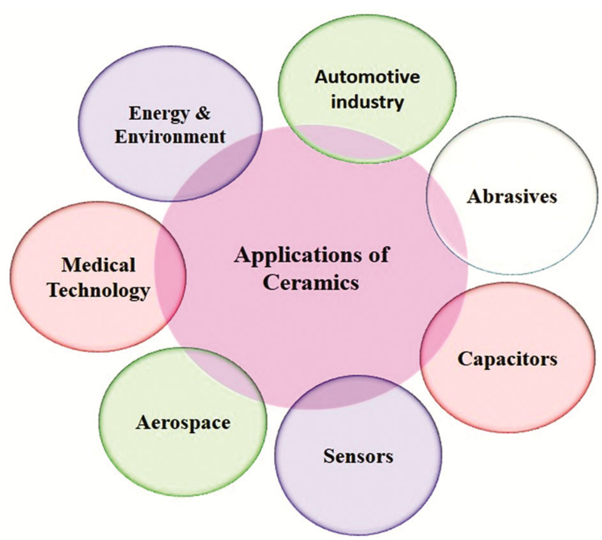

Fig. 1 — Applications of ceramic materials.

*Corresponding author: (E-mail: kumarrrpi@gmail.com)

tetragonal and cubic. The monoclinic phase has C_{2h}^{5} or $P2_1/c$ the space group of [8]. The tetragonal phase is found to have D_{4h}^{15} or $P4_2/nm$ space group[9]. Further, the cubic phase has the space group of O_h^5 or Fm3m. ZrO_2 is one of unique transition metal oxide which has excellent optical properties attribute to the great contribution in optical engineering. ZrO_2 is known to have catalytic characteristic in dehydration and hydrogen exchange reactions. It is considered to have acidic as well basic nature[10]. ZrO_2 is one of the most promising oxide material among the class of functional and structural materials due to its excellent properties high refractive index, suitable for active wave guide sensors and coatings of optical filters in UV to IR region and low absorption. ZrO_2 thin films can be synthesized using high vacuum techniques such as RF sputtering, atomic layer deposition (ALD), electron beam evaporation, pulsed laser deposition, and sol- gel (significant and low-cost technique)[11]. The nanosized ZrO_2 powder samples can be synthesized using chemical route such as co-precipitation, solvothermal/hydrothermal, combustion and solid-state reaction method *etc.*[12-14]. The electrical, structural, optical and morphological properties of ZrO_2 thin films are investigated for insulating layers in electronic applications. ZrO_2 is also named as ceramic steel due to its optimum properties for dentistry. The biocompatibility, fatigue resistance, good wear properties, high fracture toughness and radiopacity of zirconium oxide make its use in dental bridges, crowns, inserts and implants[15]. The mixing of Al_2O_3 and Ga_2O_3 with the zirconium oxide changes the structural, catalytic and absorption properties of its surface. The mixed oxides based zirconium oxide influence its electron acceptor properties which defines how the surface properties are related to its catalytic activity[16]. ZrO_2 has been considered as the promising material because of its promising properties such as wide band gap, high-κ dielectric (~27) and chemical inertness to acid and base solution. Moreover, Zirconium oxide crystals have high melting point (~2700 °C) and high Mohs hardness (>8). In practice, high-κ zirconium oxide is processed using low temperature technique that is used as significant gate insulator in high- resolution flexible display assembling[17]. Miyajima *et al.* reported the catalytic behaviour of gas phase ZrO_2 clusters with NO and CO analyzed by post heating treatment[18]. The thermoluminescence (TL) study on ZrO_2 makes it useful for producing TL dosimetry detectors of different types of ionizing radiations. TL study of bulk and nanocrystalline zirconium oxide exposed to different types of radiations such as X-rays, gamma (γ) radiation, UV radiation, low and high energy ion irradiation, neutron and beta (β) radiation that are discussed in literature[19]. The ZrO_2 thin films are used as UV dosimeters in personal or environmental dosimetry[20]. In 90s decade, zirconium oxide undoped and doped with different activators were successful investigated the TL response under UV and visible light irradiation. Thermoluminescence TLD pellets based on zirconium oxide are used in medical physics[21]. Zirconium based alloys are used in nuclear applications such as nuclear fuel cladding, light weight reactors (LWRs), Pressurized Water Reactors (PWRs) and removal of toxic metals for water treatment purposes[22,23]. US nuclear Navy unit developed the first zirconium based alloys in 1950 for the usage of nuclear fuel cladding[24]. Pouchon *et al.* reported the temperature dependent study of thermal conductivity of ZrO_2 based inert-matrix fuel (IMF)[25]. Zircaloy-4 and E110 zirconium based alloyed were used in Russian and Western reactors plants[23]. The demonstration of structural response of oxide nanoceramics have been reported in ceria (CeO_2) and zirconium oxide (ZrO_2) and bulk yttria-stabilized zirconium oxide (YSZ) thin films[26-29].

2 Motivation of the review

The motivation of this review paper is to discuss the different properties, synthesis and applications of ZrO_2. The subject of ceramic nanostructures is wide and a large number of review articles have been published but zirconium oxide constitutes a special niche of nanostructures because of its great interest of the scientific community in ceramics. This review deeply focuse on different properties of zirconium oxide such as phase transition (structural), morphological, optical, mechanical, electrical, catalytic and its stabilization *etc*. The various chemical and physical routes of synthesis have been discussed: Co- precipitation, sol-gel, solvothermal/hydrothermal, RF/DC sputtering, vacuum arc deposition, inert gas condensation and atomic layer deposition *etc*. The important applications of ZrO_2 such as fuel cells, electrical devices, memory devices, dentistry, biological and nuclear applications have been discussed in details.

3 Phase transformation and various properties of ZrO_2

Zirconium oxide consists three different structure i.e. (i) monoclinic structure exists below 1170 °C, (ii) tetragonal structure exists between 1170 °C and 2370 °C and (iii) cubic structure exists from 2370 °C to the melting temperature (2680 °C) of zirconium oxide [30]. Tetragonal structure of ZrO_2 is known as important structure because it consist fracture toughness and good hardness[31].The phase transformation in bulk zirconium oxide can occur due to many factors like amount and type of stabilizer, variation in pH value, formation of defects/vacancies in anionic sub lattice, low and high energy ion irradiation[32-35]. Srinivasan *et al*. reported that the crystal structure of zirconium oxide depends upon the rate of precipitation which is observed by variation in pH range (7-11). Monoclinic structure is obtained with the rapid precipitation while tetragonal structure is obtained with the slow precipitation (8 hours) in this pH range. But the pH value of (approx. 13) provide only tetragonal structure from both fast and slow precipitation[36]. Balasaritha *et al*. reported the monoclinic to tetragonal phase transition upon 60 keV Kr ion irradiated of zirconium samples synthesized by using the thermal decomposition technique[37]. Sharma *et al*.[35] reported all three phases of zirconium oxide thin films i.e. monoclinic, tetragonal and cubic and investigated the monoclinic to tetragonal phase transformation under 120 MeV Ag swift heavy ion beam irradiation. A.G. Balogh reported the monoclinic to tetragonal phase transition of ZrO_2 samples synthesized by inert gas condensation technique. The prepared samples were sintered at 900 °C and 1000 °C and irradiated with 4 MeV Kr^+ ions with the range of fluence 2×10^{15} ions/$cm^2$to 2×10^{16} ions/cm^2. Simultaneously, ion irradiation leads to the formation of defects and defects density increased with increasing ion irradiation dose[38]. The phenomenon of phase transition of zirconium oxide produced by different techniques is summarized in Table 1.

a. Structural Properties

The demands for the improvement in the performance of the systems for various potential applications require the investigation of structural and other properties of the materials. The crystal structure, phase identification, strain, stress, texture coefficient, crystalline quality, dislocation density, crystallinity, and crystallite size of synthesized ZrO_2 nanoparticles can be investigated using the diffraction patterns obtained from X-ray diffraction (XRD) spectra[46,47]. Aysar S. Keiteb investigated the monoclinic structure of ZrO_2 nanoparticles prepared by thermal treatment technique using the metal precursor (zirconium (IV) acetate hydroxide) and capping agent (polyvinylpyrrolidone). The increase in calcination temperature of ZrO_2 nanoparticles from 30 °C to 900 °C cause the increase in intensity and narrowing of the diffraction peaks which signify the increase in crystallinity of ZrO_2 nanocrystals[48]. Danna *et al*. also investigated the tetragonal and monoclinic phase of zirconium oxide nanoparticles with the particle size in the range of 15-18 nm prepared using co-precipitation method[49]. Zirconium oxide nanoparticles prepared using hydrothermal method obtained in monoclinic and cubic structure upon calcination at 400 °C ZrO_2 crystallized using calcination technique exhibited tetragonal structure and microwave hydrothermal method processed exhibited monoclinic structure when heated at 600 °C[50,51]. Also, the evidence of formation of ZrO_2 nanocrystals by microwave combustion method was investigated by transmission electron microscopy (TEM). The TEM study describe the uniform spherical shape and good crystallinity of the nano-crystals and selected area electron diffraction (SAED) pattern that assures the tetragonal structure of ZrO_2 samples[52]. Moreover, the crystal

Table 1 — Summary of the phase transition of ZrO_2 synthesized by different techniques.

S.No.	Material	Synthesis method	Transition factor	Phase transition	References
1.	ZrO_2	Precipitation method	Temperature Variation	t→ m	[39]
2.	ZrO_2 (thin films)	PLD	135 MeV Ni ion beam	m→ *t*	[40]
3.	ZrO_2	Thermal decomposition	Temperature Variation	t → m	[41]
4.	ZrO_2 (bulk)	Thermal hydrolysis	Calcination	c→ t, t→ m	[42]
5.	ZrO_2 (thin films)	PLD	200 MeV Ag-ion beam	m→ *t*	[35]
6.	ZrO_2 (thin films)	Sol-gel dip coating	Annealing time	t→ m	[43]
7.	ZrO_2 (thin films)	Sol−gel deposition	Temperature Variation	a→ *t*	[44]
8.	ZrO_2 (thin films)	Spin-coating	Solute – Conc. Variation	t→ m	[45]

structure, defects and chemical composition of the materials can be characterized by XRD, RAMAN, IR, TEM and SEM. The zirconia with cubic crystal structure exhibits high index of refraction and it is used in gemstones and diamond simulant in jewellery. Further, the cubic structure of zirconia with low thermal conductivity is used as thermal barrier coating in jet and diesel engines that permits the operation even at high temperature[53]. Yttria-stabilized zirconia (YSZ) is used in ceramic crown restorations[54].

b. Morphological properties

The optical, electrical and structural properties of nanostructured metal oxide materials strongly depend upon their morphology and their morphology depend upon the method of synthesis. Therefore, it is important to study the morphology of metal oxide for potential applications. Materials are synthesized in different shapes, size and crystalline structures that are used for different implications. Among different shapes, 1-D nanostructured materials with very excellent properties have applications in LEDs, sensors, solar cells, supercapacitors *etc*.[55]. Authors have reported the different shape and size of ZnO, TiO_2, SnO_2, MgO, HfO_2 and Al_2O_3 *etc*. metal oxide nanoparticles. Moreover, nanobars and hexagonal-shaped nanodiscs of ZrO_2 nanostructures were synthesized hydrothermal route at different synthesis parameters. These nanostructures confirmed the monoclinic structure (m-ZrO_2) with crystallite size of 25 nm[56]. Zirconium oxide can be immobilized by increasing the surface to volume ratio and decreasing the size of nanoparticles[57]. Luminescence can be generated in biomineralized zirconium oxide by binding peptides[58]. Waghmare *et al.* reported the bigger clusters of ZrO_2nanopowder due to increase in crystallite size. Further, EDX spectra represents the atomic weight % of the samples after annealing at 650 °C, 750 °C and 850 °C[59]. Zirconium oxide nanorods/microrods were prepared using solvothermal technique at 200 °C with different heating time (24 h, 72 h and 96 h). The reported nanorods are mixed and linked nanorods of ZrO_2, where each linked nanorods is composed of two linear assembled nanorods[60]. ZrO_2 nanorods have implications in humidity sensing. Its mechanism is discussed by Wang *et al.* using complex impedance spectra[61]. AFM is a very-high-resolution type of scanning probe microscopy that is used for 2-D and 3-D imaging of the morphology of thin films. Thaveedeetrakul *et al*. reported the homogeneous, uniform nanostructure of ZrO_2 thin films (target to substrate distance less than 60 nm) formed on 316L-stainless steel type substrates using dual cathode DC unbalanced magnetron sputtering. Different samples were formed based on the variation in target - to - substrate distance ($d_{t\text{-}s}$) 60 to 120 nm. It was observed that average grain size (~15-25 nm) and surface roughness (~5-3 nm) decreased with increasing $d_{t\text{-}s}$[62]. Also, AFM study determine the parameters i.e. skewness and kurtosis that define the asymmetry and the flatness of the surface distribution respectively.

c. Optical Properties

Zirconium oxide has large optical band gap (~5.5), low absorption coefficient, high refractive index (2.1-2.2), high opacity in visible and IR region and absorption of photons with direct and indirect interband transitions[63-66]. It is considered that the aspect of material’s toughness is related to the damage threshold in rain erosion[67]. The high toughness (~3.9 MPa $m^{1/2}$) of zirconium oxide is useful to work as protective layer for optical implications. The significance of optical properties of ZrO_2 finds its various technological applications including broadband interference filters, optical sensors, high reflectivity mirrors, active optical devices and various transparent optical components[63,68,69]. The stack of the layers on mirrors and antennas embedded in aircrafts consist some active component such as filters. These layers are optically and electrically tunable and affirm the effectual UV- visible and IR transmission of radiations. An upper layer of the stack protects the device to be stressed and aggressed from external natural occurring phenomenon such as rain erosion[70]. The high opacity of zirconium oxide is widely demanding for dental applications[71,72]. Optical transmittance and reflectance spectra of ZrO_2 thin films deposited by DC magnetron sputtering have been used to determine the optical band gap, refractive index and extinction coefficient of the samples[73].

The optical direct band gap energy of ZrO_2 nanoparticles is reduced from 4.83 eV to 4.74 eV as a function of calcination temperature (600 to 900 °C)[48]. Moreover, the indirect band gap was determined in the range of 5.6 to 5.73 eV for pure and annealed samples at temperature (300 °C, 500 °C and 700 °C) that synthesized using spin coating techniques[74].

Kumari *et al.* studied the optical properties using optical absorption and photoluminescence (PL) spectroscopy of ZrO_2 nanostructure synthesized by hydrothermal method[75]. However, few report are available on PL properties of zirconium oxide, although PL emission spectra has been observed using the excitation wavelength of 254 nm and 412 nm for zirconia nanoparticles synthesized by microwave irradiation technique[76]. PL emission spectra was obtained for ZrO_2 samples annealed at 850 °C, 1250 °C and 1450 °C when excited with wavelength 297 nm. The emission peak centered at 499, 510 and 527 nm and less intense emission band was observed at 375 nm. The observed change in peak position indicates the small change in band gap of the material[77].

The enriched luminescent properties of zirconium oxide are widely employed for photonic system. Wide band gap and short-wavelength PL emission be can be employed for compact disk read heads[78,75]. Luminescent materials have wide range of interest in various implications such as CRT lamps, vacuum fluorescent, electroluminescent and colour plasma display device[79,75]. Wide optical band gap and short wavelength luminescence emission properties of zirconium oxide nanostructures can be used in photonic applications.

d. Electrical properties

The active research towards high dielectric constant materials is constantly increasing to enable the downscaling of ultra-large scale integrated circuits and involve their implications in MOS devices as a gate dielectric material and storage capacitor in DRAM devices. There are few materials consisting high gate capacitance, low leakage current, good thermal stability such as $SrTiO_3$, Ta_2O_5, Al_2O_3, ZrO_2, and HfO_2[80]. Particularly, ZrO_2 is one of the promising candidate that consist high dielectric constant (~25), wide optical energy band gap (~4.6 – 7.8 eV), low – leakage current, high permittivity and good thermal stability. ZrO_2 is invariant with high thermal expansion ratio in FET devices. The figure of merit of high dielectric material is judged by equivalent oxide thickness (EOT) = $(k_{SiO2}/k_{high\text{-}k})dk$. The replacement of SiO_2 can increase the dielectric layer thickness with same gate capacitance. Zirconium oxide is excellent in multiple gate FinFETS and lots of electrical device work focus on this promising material[81]. Dielectric constant and dielectric loss of ZrO_2 samples *calcined* at different temperature. At higher frequency region, dielectric constant as a function of frequency, decreased due to decrease in polarization effect. The value of dielectric constant was found to be 8,38, 10 and 7 for the sample calcined at 400, 600, 800 °C and 1100 °C for the frequency value of 5 MHz. The decrease in dielectric constant in range of 600 to 1100 °C consisted with variation in crystallite size as large as expected. High dielectric constant of the samples, ascribed to space polarization effectat low frequency region. The decrease in dielectric loss with increase in frequency also ascribed to space polarization effect. The constant dielectric loss behaviour indicates the lossless nature of the materials which can be used for high frequency applications[82]. Choi *et al*. reported the low current through ZrO_x gate fabricated layer by low temperature solution technique in organic thin films transistors (OTFTs) *i.e.* Al-ZrO_x-Au. They reported the decrease in leakage current by 1000 times with increase in thickness by 2.3 times, 8.8x10-5 A/cm^2, 5.0x10-7 A/cm^2 and 8.0x10-8 A/cm^2 at 1 MV/cm for the thickness 30, 50 and 70 nm respectively[83].

e. Mechanical Properties

The information about the mechanical properties of zirconium oxide would facilitate the advancement of technology of these materials and explore the studies on their resistance to mechanical strength mechanism under different conditions. In general, Zirconium oxide consist high fracture toughness, thermal shock and wear resistance and good mechanical strength[84]. The zirconia toughened ceramic materials includes the dispersion of zirconia particles with the matrix of another ceramic materials like Al_2O_3 and partially stabilized zirconia. The complex microstructure of toughened zirconia ceramic is developed by heat treatment method of zirconia- rich solid solution[85]. Shimizu *et al*. reported that the zirconium oxide can retain the bending strength (BS) greater than 700 MPa. Also, they studied that no significant time dependent changes were observed for 3 years in bending strength of ZrO_2[86]. Yttrium oxide partially stabilized zirconium oxide (YPSZ) evolves a new class of ceramic material exhibit better toughness as compared to alumina. Christel *et al.* reported the high bending strength ranging from 900-1200 MPa, density (6 g/cm^3), Young's modulus (200 GPa) and improved 10 MN/m$^{3/2}$toughness[87]. Vasylkiv *et al.* reported that bulk nanostructured 3-mol%-yttria-stabilized zirconium oxide (YSZ) ceramic shows the hardness of

12.2 GPa with the efficient fracture toughness (9.3 $MPa.m^{1/2}$)[88]. The remarkable mechanical properties of zirconia encourage its clinical use for various purpose. The small amount of addition of Al_2O_3 to Yttrium oxide -stabilized tetragonal zirconium oxide polycrystals (Y-TZP) is known to enhance the tensile deformation and improved toughness. Sakka *et al.* studied the superplastic properties of zirconia- and alumina-based nanocomposites and observed that the tensile ductility enhanced 300% at initial strain rate of 1.2×10^{-2} s^{-1} at 1723 K with addition of alumina [89]. Zirconium oxide silica nano-fibers are used for dental purpose because of their high reinforcement. Incorporation of these nano-fibers increased the modulus of rupture, fatigue resistance and fracture strength of composite materials. The zirconium oxide silica nano-fibers were synthesized by using electro-spinning method then amalgamated into feldspathic ceramic using milling technique. The fracture toughness of prepared samples of 2.5 and 5 wt% nano-fibers were more significant as compared to the samples of 7.5 weight%[90]. The most extensively used stabilizers are lime (CaO), magnesia (MgO) and yttrium oxide (Y_2O_3). Magnesia-PSZ has many excellent properties which is used in tribological material and it is as known very hard ceramic as compared to metals[85]. Magnesia Partially Stabilized Zirconia (Mg-PSZ) is used to replace many materials like metal alloys, tungsten carbides in industries due to its excellent properties.

4 Stabilization of zirconia

The stabilized zirconia has wide range of application. Zirconium oxide can be stabilized using different materials such as magnesium oxide stabilized zirconia, yttria stabilized zirconia, indium stabilized zirconia, calcium oxide stabilized zirconia and *etc*. Yttria-stabilized zirconia (YSZ) has been widely used in thermal barrier coatings (TBCs) to safeguard the metallic parts from high temperature in gas turbines that provide substantial benefits to the engine. The corrosion resistance of zirconium oxide coatings can be improved by employing the different stabilizers except yttria because stabilizer plays an important role in corrosion resistance of TBCs[91]. Jones *et al*.[92] selected the In_2O_3 (7.8–12.2 mol% $InO_{1.5}$ - stabilized zirconia) stabilizer instead of Y_2O_3 and found the improved corrosion resistance in gas turbines burning low quality fuels. The fracture toughness of yttria- stabilized tetragonal zirconia is high and its crystal structure is transformed form tetragonal to monoclinic structure with a 4% volume expansion on applying stress: known as stress induced phase transformation. Tanaka *et al* reported the mechanical properties of partially stabilized zirconia (PSZ) for dental implications[93]. Nawa *et al.* developed the ceria based stabilized tetragonal zirconia nanocomposite ceramic material which was found to have high fracture toughness and good resistance to low temperature deterioration[94]. Denti *et al*. compared the yttria – stabilized zirconia in colored and natural five shades. The observed changes in the samples after polishing and their recovery after annealing also have been introduced. It was concluded that the Y-TZP is a promising material for fixed dental prostheses due to its outstanding aesthetical and mechanical properties[95]. The addition of magnesium chloride alters the properties of stabilization of zirconia. XRD and SEM techniques were used to investigate the phase and microstructure of stabilized zirconia and mechanical properties were investigated by three point bending and microhardness tests[96].

5 Chemical Synthesis techniques

a. Co-precipitation method

It is reported that the nanoparticles synthesized via co-precipitation method contain captured water molecules in the lattice because of fast growth of NPs in chemical reaction in an aqueous solution. Co-precipitation is the method which is carried down by the formation of precipitates of substances generally soluble under the applied conditions. This method is used to get the uniform composition in two or more cations homogenous solution through precipitation reaction. During the method, there are four basic simultaneous process *i.e.* nucleation, growth, coarsening and agglomeration[97]. Some reports are available on synthesis of metal oxide nanoparticles such as ZnO, TiO_2, VO_2, MoS_2, HfO_2, Al_2O_3, WO_3 and SnO_2 using coprecipitation method[98]. Here, nucleation is the key process where large numbers of small particles are synthesized. Pure ZrO_2 nanoparticles of tetragonal phase were synthesized using the ammonia solution and precursor ($ZrCl_2O.8H_2O$)[99]. Nanocrystalline zirconia can be stabilized using coprecipitation synthesis technique with adding some dopants such as MoO_3, WO_3, $TaO_{2.5}$, and $NbO_{2.5}$ *etc*. The comparison of azeotropic distillation, ethanol washing and freeze drying were done for the gels. It was observed that 9 mol% of

$InO_{1.5}$ plus charge-compensating dopants is sufficient for complete stabilization of high temperature phase of ZrO_2 as analyzed using XRD and raman techniques. The improvement in specific surface area and crystallite size were obtained through treatment of ethanol washing and azeotropic distillation[91]. Arsent'ev *et al*. reported the synthesis of ZrO_2-CeO_2 nanoparticles using coprecipitation method and Rossignol *et al*. reported that the structure and texture of ZrO_2 nanoparticles depends upon the synthesis method and type of precursor used[100,101]. MgO-ZrO_2 nanoparticles were synthesized for the antibacterial application and it was reported that the mixed NPs can be used to treat infectious disease caused[102].

b. Microwave- assisted synthesis

Microwave synthesis is very interesting technique for synthesis of nanomaterials. Microwave radiation helps in achieving the rapid heating in reaction system which increase the reaction and decrease reaction time by increasing reaction kinetics. In this technique, microwave radiations are absorbed by solvents possessing high dielectric constants and produces high heat. Uniform heat is obtained in reaction mixture through dipole-diploe interactions by alternation electric field (EF) provided by microwaves which provide homogeneous nucleation and growth kinetics in solution. Hence, microwave energy is more efficient and need less energy and time in synthesis of nanoparticles as compared to other conventional heating techniques[103]. This technique has emerged as an economic tool for control over particle size and dissolution enhancement. The ability of microwave radiation has been found substantial due to direction reaction with the molecules and formation of thermal conductivity in quick span and time[104]. The synthesis of pure cubic zirconium oxide nanoparticles is a challenging task. Manjunatha *et al*. reported the pure cubic structural phase of ZrO_2 using microwave assisted synthesis technique and studied the optical and photoluminescence properties. The pore size of the ZrO_2 nanoparticles found to be decreased with increase in calcination temperature. The photoluminescence spectra showed the intense violet emission ascribed to the presence of oxygen vacancies in zirconium oxide matrix[105].The tetragonal structure of ZrO_2 nanoparticles were obtained by microwave synthesis using zirconium acetate hydroxide with different concentration of Poly vinyl pyrrolidone. The properties of synthesized nanoparticles were studied using XRD, SEM, TEM, and Raman spectroscopy[106].

c. Sol-gel process

The sol-gel process is well-established elegant chemical route to synthesize novel metal oxide nanoparticles as well as mixed oxide composites and low temperature synthesis of single or multiple component ceramic materials. This method has potential control over textural and morphology of complete reaction during the synthesis of solid. Sol-gel method mainly undergoes in four steps to deliver the final product and those are hydrolysis, condensation, and growth of particles, gel formation and drying[107]. Sol-gel synthesis of metal oxide nanoparticles is based upon hydrolysis and condensation/dehydration of the metal alkoxide, $M(OR)_n$, where M, O, R and n denotes for metal, oxygen, organic group and number of repeated units respectively. In a condensation reaction, two hydrolyzed molecules link together and result in M-O-M with release of water and alcohol molecule.

Hydrolysis:

$$M\,(OR)_4 + H_2O \rightarrow HO - M(OR)_3 + R - OH \quad \ldots (1)$$

Condensation/dehydration:

$$2HO - M(OR)_3 \rightarrow (OR)_3\,M - O - M(OR)_3 + H_2O \quad \ldots (2)$$

The kinetics of hydrolysis and condensation reactions are controlled by the ratio of water to alkoxide (R). The value of R decides the formation of type of product, ($R<3$) is suitable for fiber and thin films synthesis and ($R>3$) form powder particles[108]. Lim *et al.* fabricated the ZrO_2 thin films as a dielectric layer using surface sol - gel method for application of polymer field effect transistors (PFET). They reported the ZrO_2 thin films with high dielectric strength, low voltage and high – mobility for PFET[109]. Kumar *et al.* synthesized the ZrO_2 nanostructures using the sol- gel method. The calcination temperature changes the structural, optical and thermal properties of ZrO_2 nanostructures of mixed monoclinic and tetragonal phase. The spherical particles with nano size distribution (8 nm) were obtained when samples calcined at 500 °C. While the calcination at 600 °C provided the increase in particle size (17 nm) and at 700 °C, the ZrO_2 nanorods of width 10 nm were obtained[110].M. R. H. Siddiqui reported the effects of $ZrOCl_28H_2O$ and $Zr(SO_4)_2.H_2O$ precursors on structure and morphology of ZrO_2 nanoparticles synthesized by sol-gel method[111]. This method is influenced by synthesis parameters such as reactants, temperature, concentration and pH and presence of additives. The advantages associated with this methodology involve the lower processing temperature, high purity, control over dopant, synthesis of multicomponent composition and densification obtained at lower temperature as compared to other traditional techniques[112].

d. Solvothermal/Hydrothermal synthesis

Solvothermal method of synthesizing the nanostructure materials (metals, metal oxides, ceramic oxides *etc*.) has been developed in last decade and it is known as versatile method for precise control of morphology of nanomaterials. This method is very simple and similar to hydrothermal method except that the precursor solution is non-aqueous. The solvothermal synthesis is performed in sealed stainless autoclave where the boiling point (BP) of the solvent can be exceeded with the temperature by increasing the autotgenous pressure[113]. The synthesis using the water as solvent is known as hydrothermal synthesis. The solubility and reactivity of the reagents is encouraged by increasing the temperature and pressure which can perform the complex/unexpected reactions and improve the crystallinity of synthesized materials as compared to classical methods. The variation in experimental factors (reaction temperature, properties of solvent, reaction time *etc*.) controls the nuclei formation and growth of crystals[114]. ZrO_2 nanoparticles were synthesized by hydrothermal method using the aqueous solution of $ZrO(NO_3)_2$ and $ZrOCl_2$ at different temperature in presence of H_2O_2. Hydrothermal method of Zr salts (0.25 and 0.50 mol L-1) prepared nanocrystalline monoclinic ZrO_2 powders with small particles with size of 3.5 nm determined using TEM and XRD[115]. The crystal structure of ZrO_2 nanoparticles were controlled using solvothermal process using different organic solvents (oleic acid, benzyl alcohol and octyl alcohol) and adjusting zirconium precursor concentration (0.25, 0.50 and 0.50 mol L^{-1}). The confirmed synthesis of pure ZrO_2 monoclinic, cubic and tetragonal structure was reported. The reported results signified that the acidity of solvent can play important role for controlling the growth of zirconia nanocrystals[116]. The pure monoclinic zirconium oxide was obtained using solvothermal technique in benzyl alcohol with different Zr precursors and noticed that the release of strong acid in synthesis process is the key step to control the structure. Many methods suffer the synthesis of mixed ZrO_2 structure and require high temperature and long reaction time. The problems depend on different synthesis parameters such as selection of synthesis process, precursor solution, pH variation, presence/absence of pressure *etc*.[117].

6 Physical synthesis technique

a. Sputtering

Sputtering is a vacuum based physical vapour deposition technique which is used for the deposition of thin films on large scale to obtain the proper stoichiometry of thin films from target material. In this technique, the momentum is transferred to the atoms ejected from the target materials (alloy, ceramic or compound) by ion bombardment. The sputtering involves direct current (DC) sputtering, pulsed DC, radio frequency (RF) sputtering. Sputter deposition takes place when plasma of inert gases like Ar is formed between the electrodes by the collision of electrons to the gaseous molecule. The potential between the electrodes accelerates the ion presented in plasma, ion with sufficient energy strike to the target leads to ejection of material and then transported and deposited on the substrate[118]. ZrO_2 thin films were grown on Si substrate by DC sputtering using Zr target in Ar-O_2 atmosphere. Various characterization techniques were used for investigation of stoichiometry, structural, optical and chemical properties of the deposited thin films. The investigation of the properties was carried out with different oxygen flow rate (0-3.5 sccm)[119]. Electrical properties of RF sputtered zirconium oxide thin films were investigated for memory device applications. The device Al/ZrO_2/Pt showed the reproducible resistive switching behavior traced over 100 times at room temperature (RT). The device was fabricated with pt as bottom electrode and Cu, Ni, Ag, Al, Ti, and even W-probe as top electrodes. Besides, Ti/ZrO_2/Pt device can be operated at over 2000 switching cycles at 85 °C by sweeping DC voltage, the memory states demonstrated high stability under read voltage stress at RT and 85 °C[120]. Prabakar *et al*. studied RF magnetron sputtered ZrO_2 dielectric layers for MIS capacitor. The desirable high temperature annealing improved the electrical properties of zirconium oxide gate dielectric layers with decrease in interfacial traps at ZrO_2/Si interface[121].

b. Pulsed Laser deposition

Pulsed laser deposition (PLD) is another vacuum based physical vapour deposition (PVD) technique that employs a high power laser beam (obtained either from excimer laser or Nd: YAG laser) inside the vacuum chamber to remove the material from the target material. When the laser beam strikes to the target, leads to the melting of the target material further evaporation and ionization of the target material takes place. The atoms and molecules that ablated from the surface of the target materials deposit on the substrate. PLD technique is used for the deposition of several materials involving polymers, metal oxides, ceramics, carbides and nitrides *etc*.[122]. Balakrishnan *et al.* reported the growth of nano structure of tetragonal zirconium oxide thin films using pulsed laser deposition. The atomic force micrographs showed the formation of dense grains in pristine films and cluster formation in annealed samples. The zirconia later showed the lattice fringes and possessed the tetragonal structure with no other structure at interface and amorphous alumina. The cross-sectional transmission electron microscopy of annealed films with the thickness 5:10 nm exhibited the interdiffusion of layers at the interface[123]. The ZrO_2 thin films were grown on Zr-based alloy substrates using pulsed laser deposition technique and the effect of substrate temperature 300, 573 and 873 K studied on deposited samples. ZrO_2 thin films were not observed with good adherence for deposition carried out at 300 K substrate temperature. The deposited thin films were initially in amorphous phase with small deficiency of oxygen. The samples deposited at higher temperature were found to be good adherent with the substrate. The nanocrystals were evolved with the crystallization of monoclinic and tetragonal structure[124]. Al-Kuhaili *et al.* reported the effect of annealing on PLD ZrO_2 thin films. The surface of the samples improved with increasing in annealing temperature with increase in root-mean-square roughness. The annealed thin films exhibited the band gap in range of 5.17 – 5.30 eV[125]. Schematic diagram of the PLD technique with in situ substrate motion and optical spectroscopy is well described[126].

c. Vacuum arc deposition

The vacuum arc deposition is a vacuum based physical vapour deposition process where electric arc is used which is high current discharge operates at low voltage. Basically, vacuum arc is a highly ionized plasma gas discharge between two metallic electrodes in vacuum. The discharge burns in ionized vapour of cathode material concentrated at 1-10 µm on cathode surface. In this process, vapors are evaporated from the electrodes and ionized by discharge leads to formation of plasma. Furthermore, plasma generates a coating of the electrode material. Researchers have reported the synthesis of ZrO_2 thin films using vacuum arc deposition (VAD) method. ZrO_2 thin films have been grown on glass and Si substrate using filtered cathodic vacuum are deposition method by Martin *et al.*[127]. Amorphous to monoclinic phase transition occurred by changing the applied bias voltage from 0 to 400 V. Optical refractive index also increased (2.09- 2.22) with the phase transition. Similarly, the micro hardness of the sample increased form 11 – 16.5 GPa with the bias voltage. Optical properties of filtered cathodic vacuum arc (FCVA) deposited ZrO_2 thin films have been studied. The deposition rate of the thin films varied from 75 to 35 nm min^{-1}. The transmittance and band gap increased and optical constant decreased with increase in oxygen flow rate from 10 to 98 sccm. The film homogeneity increased with the oxygen flow rate and optical properties exhibited good homogeneity above the flow rate of 50 sccm, structure of all the samples remain same during all deposition[128]. Yu *et al.* reported the structural, elemental composition, surface morphology, optical and mechanical properties of ZrO_2 thin films deposited using FCVA technique[129]. The increase in oxygen flow rate caused the amorphous to monoclinic phase transformation with varied preferred orientation. Again, amorphous structure is obtained by increase in O/Zr atomic ratio with a conversion of Zr ions to Zr^{4+}. This change is the structural trend raised from the change in properties of the material. Amorphous samples exhibited small clusters and smooth morphology with lower hardness as compared with the crystalline samples.

d. Inert gas condensation

Inert gas condensation (IGC) is the first and easiest method for synthesis of nanoparticles. This technique employs the evaporation of materials in a cool inert gas (*e.g.* He or Ar) at low pressure followed by the condensation. A convective flow of inert gas passes over the evaporation source and carriages the nanoparticles towards liquid nitrogen cooled substrate. The breakdown of the source material to the atomic level can be done with solid or gas sources. The size and morphology of the nanoparticles is determined by the nature of the inert gas. Many research groups reported the deposition of nanocrystalline thin films using IGC technique[130,131]. In gaseous phase, method of synthesis is divided two category i.e. physical vapour deposition (PVD) and chemical vapor deposition (CVD). PVD involves the condensation in inert gas[132].

e. Atomic layer deposition (ALD)

ALD is a thin films deposition technique which is based on sequential use of gas phase chemical process. It is also known as subclass of CVD technique. On major scale, the ALD reactions use two chemicals called reactants which react with the surface of a material one at a time in a sequential, self- limiting, manner. Slowly, a thin film is deposited through the repeated exposure to separate the reactants. Also, ALD is considered a variable technique for growth of functional, passivating and encapsulating layers on halides perovskites. Study in the area of metal oxides have been focused, despitea large number of materials can be deposited using ALD technique[133]. This technique can be used to deposit the thin films of different elements, oxides, nitrides, sulfides *etc*. Semiconductor and energy conversion technologies are prominently using ALD technique. ALD has advantages over the deposition techniques because of its good conformality and control over thickness and composition of the materials. The desirable properties of the materials originate form cyclic and self- saturating nature of ALD processes. The uniform growth on high aspect ratio structures depends upon the subsequent cycle, CVD and PVD may suffer the non- uniformity of the films cause of shadowing effect and faster surface reactions[134]. Wang *et al.* deposited the zirconium oxide thin films with the tetrakis (dimethylamido) zirconium (IV) and water using atomic layer deposition (ALD) process. The growth characteristics and mechanism of ALD grown zirconium oxide thin films were investigated in the temperature range of 50–275 °C. The growth rate of thin films decreased linearly with increasing the temperature 50 °C (1.81 Å/cycle) and 225 °C (0.8 Å/cycle). The deposition of the films ceased at a temperature more than 250 °C with certain number of ALD cycles. The deposited thin films showed the different nanostructures when deposited with different number of cycles with variable temperature, observed using atomic force microscopy[135]. ALD technique was used to fabricate the ZrO_2 based metal insulator semiconductor device on SiO_2/Si substrates[136]. Hydrogen free ALD process was used to deposit the ZrO_2 thin films (15-36 nm thickness) with the temperature in the range of 220–500 °C. The ALD deposition rate decreased when the temperature increased towards higher temperature. The Al/Ti/ZrO_2/TiN/Si and Al/Ti/ZrO_2/SiO_2/Si capacitors with zirconium oxide layer grown with ALD technique, explained the dielectric behavior (15–24) and breakdown fields 1–3 MV/cm[137].

7 Applications of Zirconium oxide

The spectrum of various applications of zirconium oxide includes its coverage in crowns, dentistry, catalysts, ceramics, and replacement of SiO_2 to ZrO_2 as high-k dielectrics for devices, metal–oxide–semiconductor technology, capacitors, hard and protective coatings, diffusion barrier coatings in nuclear energy reactors, nuclear reactors, cutting tools, microelectronics, and in optical filters, antimicrobial additives in paints, abrasive applications, oxygen sensors, implants, bridges, wear resistant applications, fuel cells, gas sensors, optoelectronics and corrosion resistant material, storage capacitor, metal–oxide–semiconductor (MOS) transistors and other device application. Some important applications of zirconium oxide have been described in present work. The prominent applications of ZrO_2 are illustrated in Fig. 2 and described in details. Moreover, stable porous zirconium oxide obtained from borohydride synthesis is found to be important for adsorption of heavy metal for industrial waste water treatment. Fig. 3 illustrates the removal efficiency of Cr(VI) or Pb(II) with different time interval that was determined to be ~10% and ~99%, respectively[23].

7.1 Fuel cells

An electrochemical cell that that converts the chemical energy of fuel (oftenly hydrogen) and oxidizing agent (oftenly oxygen) into electricity is known as fuel cell. Redox reactions are carried out to convert chemical energy into electricity. Fuel cells are capable to generate electricity continuously as fuel and oxygen are provided. The first commercial fuel cell came into existence in 1932 by Francis Thomas Bacon. Fuel cells are used for primary and backup power in remote or inaccessible areas, commercial

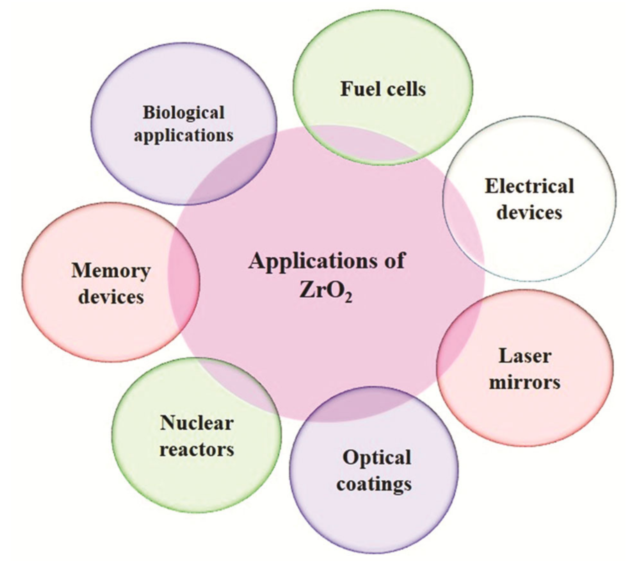

Fig. 2 — Diverse applications of zirconium oxide.

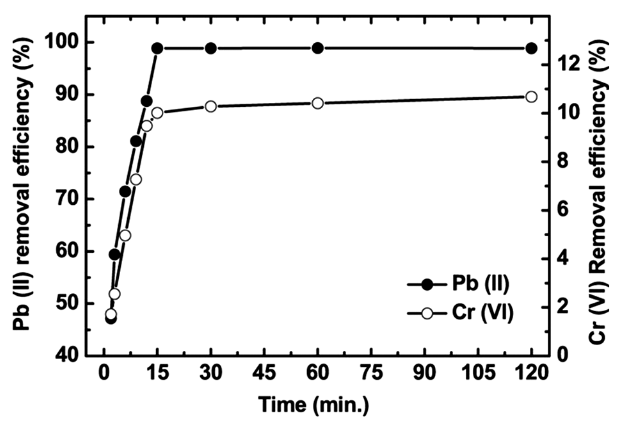

Fig. 3 — Removal percentage of Cr (VI) and Pb (II) with different interval of time. Reproduced with permission[23].

and industrial purpose, residential buildings *etc*. Fuel cells provide power to forklifts, automobiles, submarines, airplane, boats, submarines, portable power systems and fuel cell electric vehicles. In mid-1960s NASA used to alkaline fuel cells to provide power for satellites and capsules. There are many types of fuel cells such as Phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), proton- exchange membrane fuel cells (PEMFCs), electric storage fuel cell, molten-carbonate fuel cell (MCFC), direct methanol fuel cells (DMFCs), solid acid fuel cell (SAFC), and high-temperature fuel cells: Solid oxide fuel cells (SOFCs). The type of the fuel cell is classified based on the electrolyte and the startup time 1 sec of PEMFC and 10 minutes for SOFCs[138]. Two important fuel cells (DMFCs and SOFCs) are discussed here. In these fuel cells zirconium oxide is used as solid material as an electrode and electrolyte. Iannaci *et al.*[139] reported the use of sulfated zirconium oxide (S-ZrO_2) as electrode and electrolyte additive for DMFCs. They prepared the nafion electrolyte composite membranes and Pt electro catalysts using sulfated zirconium oxide at different content and the catalytic activity was investigated using voltammetry technique. Pt/S-ZrO_2 catalysts presented the improved efficiency for oxygen reduction reaction and improved methanol tolerance as compared to bare Pt. Pt/S-ZrO_2 based carbon cloth electrodes with Nafion/S-ZrO_2were used as composite electrolyte membrane in DM fuel cell. Sulfated zirconium oxide was used as catalyst and electrolyte additive provided the enhanced membrane and electrode interface stability as investigated by electrochemical impedance spectra (EIS) recorded during fuel cell operation. DM fuel cell operation was carried out using methanol solution feeding with anode and oxygen with cathode that acquired polarization and power density curves at 90 °C. The tetragonal phase of zirconium oxide is significantly used as anode in SOFCs, catalyst oxygen sensor and structural material. E. S. Elshazly[140] reported the Ni stabilized zirconium oxide SOFCs. Yttria stabilized zirconia (YSZ) electrolyte were used in solid oxide fuel cells. EIS studies of symmetrical cells were carried out using Lanthanum Strontium Manganite- Yttria stabilized zirconia (LSM-YSZ) composite electrodes. The cathodic polarization was only studied because it is higher than anodic polarization in Ni-YSZ/YSZ/LSM-YSZ cells. EIS spectra between 700 – 850 °C showed the small decrease in polarization resistance for the machined samples as compared to smooth surface samples[141].

7.2 Electrical devices

ZrO_2 is promising material for fabrication of electrical devices: very-large-scale-integrated (VLSI) circuits as well as ZrO_2 thin films are well studied in field effect transistors (FET), metal oxide semiconductor, metal insulator metal (MIM) capacitor and dynamic random access memories (DRAMs), 3D capacitors and thin-film transistors (TFTs) *etc.*[142-145]. Moreover, ZrO_2 thin films are extensively used for the optical and electronics applications. TFTs with ZrO_2 gate dielectric exhibit better performance due to high dielectric constant (~25) of zirconium oxide, produce gate dielectrics with low leakage and high capacitance density. These films exhibit properties that are different from the bulk material due to their differences in microstructure and crystalline phases[146]. Polymorphous ZrO_2 thin films may bring undesired effects on their leakage current and different anisotropic crystalline structures existed in the samples leads to non-uniformities in k value and in film thickness[147].

ZrO_2 is considered to replace the SiO_2 due to its high gate leakage current in MOSFET technology. It is essential that the high-k dielectric gate stacks withstand the high temperature of 1000 °C involved in transistor fabrication processes. Thin film metal-oxides including Al_2O_3, ZrO_2 and HfO_2 *etc*. are good materials for this usage because even at these high temperatures, they are thermally stable on Si[148]. Despite the significant research available in the advancement of ZrO_2 based TFTs, only limited studies are reported on carrier mobility and operational stability. Many present studies reported on TFTs using ZrO_2 thin films deposited on Si/glass substrate[149]. Mainly, TFTs are logical building blocks for various device applications including flat, flexible and transparent liquid crystal displays LCDs[150]. The attractive electrical and optical properties of ZrO_2 based TFTs are such as band gap tunability, multiple exciton generation, and inexpensive chemical-based low temperature techniques can be useful for mass production of large scale electronic devices at low cost[151]. Rao *et al*. reported ZrO_2 thin films based metal oxide semiconductor device[152]. Brunet *et al*. reported the nanocrystalline tetragonal metastable zirconium oxide thin films by for 3D capacitors[153]. The phase transition and microstructure of ZrO_2 thin films impacts the electrical performance of capacitors under the annealing effect at 900 °C in oxygen environment. The capacitance densities were found to be 2 nF/mm^2 and 2 nF/mm^2 for planer capacitor and for capacitors with pores etched in silicon with a 4:1 aspect ratio respectively.

7.3 Memory devices

The research interest towards the memory device technology is rapidly growing due to various applications in our daily life. The memory devices are categorized into two parts volatile and non-volatile. The technology using ZrO_2 are enhanced due to its excellent properties such as high melting point, high refractive index, high dielectric constant, low absorption from *near UV* through the *mid-infrared* (*IR*) region and good oxidation resistance. The charge trapping layer of amorphous zirconium oxide is used in flash memory devices. The germanium based non- volatile memory devices with zirconium oxide as a charged trapping layer is reported by Y. H. Wu[154]. The Al_2O_3 layer was employed as blocking layer and Al gate electrode. The ZrO_2 trapping layer provided the high permittivity of 36.8 with a large amount of trapping sites and hence a 1.8 V memory window at ±5 V program/erase (P/E) for 1 ms was achieved. Lee *et al*.[155] investigated the fabrication of flash memory that consisted Ge nanocrystals and ALD deposited ZrO_2 layer. The Ge and ZrO_2 consisted metal oxide semiconductor (MOS) capacitor with Ti/Au top electrode exhibited a 3 V memory window at ±9 V bias. Whereas, negligible memory window was determined for MIS capacitor without Ge NCs. Moreover, zirconium oxide has extensively got attention in resistance random access memory (RRAM) devices. The RRAM memory devices have great advantages including low operation power, non-destructive readout, simplicity and high integration density *etc*. Various parameters such as effect of buffer layer, electrode material, metal implantation, embedded metal layer and metal doping *etc*. effect on the resistive switching properties of ZrO_2 thin films. The I-V characteristics of RRAM device with zirconium oxide layer have been explained well. A good retention behaviour was detected for the device in high and low resistance states. The high and low resistance state was obtained 90 and 40 kΩ respectively[156].

7.4 Biological applications

The use of ZrO_2 as biocompatible materials first published in 1969[157]. Zirconium oxide is highly biocompatible in vitro and vivo studies, especially when it if free from all kind of radioactive contents. Ceramics based on ZrO_2 are chemically inert, good cell adhesion and no adverse systemic reactions association *etc*. At low temperature and from the manufacturing process, the release of particles from the degradation of zirconium oxide promotes the immune localized inflammatory reaction. It is lower toxic material than titanium oxide and *aluminium* oxide[158]. Currently, zirconium oxide is employed as femoral ball head in THR and so *in vivo* contact soft tissues and blood. Some reporters have reported that ZrO_2 showed no cytotoxic effect when fibroblast was co-cultured with it or with extract using different techniques[159]. Ito *et al*. reported the effect of L929 fibroblast co-cultured in the presence of pseudo extra cellular fluid which was used as lubricant in wear tests[160]. Current reports are available on strong variability of ZrO_2 in vivo degradation results in the strong effect of processing on ageing process. Zirconia is prone to ageing in presence of water due to its metastable structure. More than 60,000 femoral heads made from zirconia have been implanted in US and Europe. Manufacturers claimed the limited problem in vivo situation until 2001 and 400 femoral heads failed in short period. Biomedical grade zirconia is well understood and can be used as powerful tool to assess its sensitivity against ageing. Zirconia for dental implants is quite young and in development phase for dentistry[161].

7.5 ZrO_2 in nuclear applications

Historically, the demand of titanium arose for aerospace industry, similarly the ever increasing demand for zirconium oxide arose in nuclear industry. Zirconium oxide is highly preferred candidate in nuclear systems due to its alloys consist good mechanical properties, structural components for light and heavy water nuclear reactor cores, high corrosion resistance, resistance to irradiation damage, transparency to thermal energy neutrons. The wear resistance of different reactor materials compared to have a series of test with zirconia alloys (Zircaloy-2) fretted against palladium, tantalum, niobium, and austentie stainless steel. Attia *et al*. reported the improvement in the wear resistance of Zr-2.SNb alloy by use of laser surface modification with mating Zircaloy-4[161]. Zircaloy alloy of zirconia is used in fuel cladding in light water reactors due to benefit of the relatively low neutron capture cross section of zirconia. With the demand of ZrO_2 in nuclear applications, the chemical industries found it excellent candidate due to its resistance to a wide range of corrosives. In nuclear systems, the zirconium alloys are better than hafnium alloys. In nuclear applications hafnium alloys has enormous effect on absorbing thermal neutrons. Hence, zirconium alloys are appropriate for nuclear control rods that are highly in demand to absorb excess neutron to control the uranium fission process. The highly preferred reason for the use of zirconium in nuclear application is its good resistance to water and steam. The most important zirconium alloys for nuclear system are zircaloy-2, zircaloy-4, Zr–2.5 Nb, and Zr–1 Nb because of their more reliability in hot water and steam[162]. Zirconium alloys are used in 95% thermal neutron reactors worldwide in 2017. The elements of *pressurized water reactor* (PWR), water-water energetic *reactor* (WWER) and *boiling water reactor* (*BWR*) fuel assemblies (or fuel bundles) are made of zirconium alloys[163].

8. Outlook

The interest towards ZrO_2 particles has been increased due to its interesting properties and applications in diverse fields. Due to the fascinating properties of ZrO_2 among the class of ceramics like high- k dielectric, large optical band gap, high melting point and low absorption *etc*., the interest of the researchers is continuously increasing for ZrO_2 ceramics. In chemical route of synthesis, co-precipitation and sol-gel techniques are considered best for getting fine particle size. Mainly, the size of the nanoparticles depends upon the synthesis route. The XRD structure of ZrO_2 has characteristic peaks having monoclinic, tetragonal and cubic phase. The morphology of nanoparticles is investigated using SEM and AFM technique. The ZrO_2 nanorods prepared using solvothermal technique has implications in humidity sensing. Wide band gap and short wavelength luminescence emission properties are employed in CRT lamps, vacuum fluorescent, colour plasma display device and photonic applications. The high dielectric constant of ZrO_2 enables the downscaling of ultra-large scale integrated circuits and their implications in MOS, DRAM and other storage devices. Stabilized zirconium oxide has been widely used in thermal barrier coatings and dental applications. The solid ZrO_2 is used as an electrode and electrolyte in direct methanol and solid oxide fuel cells. The VLSI circuits, FETs, DRAM, TFTs, 3D capacitors, flash memory and non-volatile memory devices use the thin dielectric layer of zirconium oxide. The high preference of ZrO_2 in nuclear systems is due to its excellent mechanical properties, structural components for light and heavy water nuclear reactor cores, high corrosion resistance, resistance to irradiation damage, transparency to thermal energy neutrons. Zirconium oxide is highly biocompatible *in vitro* and *vivo* studies.

Acknowledgments

One of the author's Dr. Rajesh Kumar, Associate Professor of Physics acknowledges the Faculty Research Grant Scheme (FRGS) Project provided by Guru Gobind Singh Indraprastha University, New Delhi, India. Miss. Deepika Gupta (Ph.D Scholar) is also thankful to Guru Gobind Singh Indraprastha University, New Delhi, India, for providing the Short Term Research Fellowship (STRF).

References

1 Ferré F G, Mairov A, Ceseracciu L, Serruys Y, Trocellier P & Baumier C, *Sci Rep*, 33478 (2016) 1.
2 Yalamaç E & Basturk S B, Ceramic fibers, Fiber Technology for Fiber-Reinforced Composites, Woodhead Publishing Series in Composites Science and Engineering, (Elsevier), 1stEdn, 2017.
3 Drouet C, Leriche A, Hampshire S, Kashani M, Stamboulis A & Iafisco M, Types of ceramics: Material class, Advances in Ceramic Biomaterials, (Elsevier), 1stEdn 2017.
4 Ali M S, Ariff A H M, Hashmi S & Brabazon D, Reference Module in Materials Science and Materials Engineering , (Elsevier), 1stEdn 2018.
5 Sakabe Y, *Curr Opin Solid State Mater Sci*, 2 (1997) 584.
6 Narayan R J, Kumta P N, Sfeir C, Lee D, Olton D & Choi D, *Mater Sci JOM*, 56 (2004) 38.
7 Afshari M, Abbasi R & Sovizi M R, *Trans Nonferrous Met Soc China*, 30 (2020) 90.
8 Terki R,Bertrand G, Aourag H & Coddet C, *Mater Sci Semicond Process*, 9 (2006) 1006.
9 G Teufer, *Acta Cryst*, 15 (1962) 1187.
10 Nakano Y, Iizuka T, Hattori H & Tanabe K, *J Catal*, 57 (1979) l.
11 Boratto M H, Congiu M, Santos S B O & Scalvi L V A, *Ceram Int J*, 44 (2018) 10790.
12 Sagadevan S, Podder J & Das I, *J Mater Sci: Mater Electron*, 27 (2016) 5622.
13 Mahshad A, Morad R A & Iida B, *Iran J Chem Chem Eng*, 33 (2014) 47.
14 Gómez I D, García M A G, Bojarska J, Kozanecki M, & Rynkowski J M, *Com Ren Chim*, 18 (2015) 1094.
15 Bona A D, Pecho O E & Alessandretti R, *Mater (Basel)*, 8 (2015) 4978.
16 Burova M V, Fionov A V, Tveritinova E A, Kharlanov A N & Lunin A N, *Russ J Phys Chem*, 81 (2007) 164.
17 Wang D, Lu J, Jeon Y, Ouyang S & Xie Y, *Org Electron*, 57 (2018) 341.
18 Miyajima K & Mafuné F, *Chem Phys Lett*, 660 (2016) 261.
19 Nikiforov S V, Kortov V S, Kazantseva M G & Petrovykh K A, *J Lumin*, 166 (2015) 111.
20 Azoriân J, Rivera T, Martiânez E & Garciâ M, *Radiat Meas*, 29 (1998) 315.
21 Nieto J A, *Appl Radiat Isot*, 138 (2018) 35.
22 B Lustman, Zirconium in the Nuclear Industry, (West Conshohocken, PA: *ASTM Int*, (1979) 5.
23 Nayak A B & Nayak B B, Sci Rep, 23175 (2015) 1.
24 Rickover H G, Geiger L D & Lustman B, *Energy Res Dev Admin/Div Naval React*, Washington, DC (1975).
25 Barrier D C, *Berichte des Forschungszentrums Julien* (2005) 4188.
26 Edmondson P D, Zhang Y, Moll S, Namavar F & Weber W J, *Acta Mater*, 60 (2012) 5408.
27 Aidhy D S, Zhang Y & Weber W J, *Scripta Mater*, 83 (2014) 9.
28 Zhang Y, Aidhy D S & Varga T, *Phys Chem Chem Phys*, 16 (2014) 8051.
29 Dey S, Drazin J W, Wang Y, Valdez J A, Holesinger T G, Uberuaga B P & Castro R H R, *Sci Rep*, 5 (2015) 7746.
30 Pacheco G, Fripiat J J, *J Phys Chem*, 104 (2000) 11906.
31 Li M, Feng Z, Xiong G, Ying P, Xin Q, Li C, *J Phys Chem*, 105 (2001) 8107.
32 Stefanid G, Musi S, Grieta B, Popovic S & Sekulic A, *J Phys Chem Solids*, 59 (1998) 879.
33 Sekulic´ A & Furi K, *J Mater Sci Lett*, 16 (1997) 260.
34 Mirgorodsky A P & Smirnov M B, *Phys Rev B*, 55 (1997) 19.
35 Sharma A, Varshney M, Shin H J, Kumar Y, Gautam S & Chae K H, *Chem Phys Lett*, 592 (2014) 85.
36 Srinivasan R, Harris M, Simpson S F, Deangelis R J & Davis B, *J Mater Res*, 3 (1988) 787.
37 Balasaritha P, Amirthapandian S, Magudapathy P, Sarguna R M & Srivastava S K, *J Nucl Mater*, 508 (2018) 385.
38 Balogh A G, *Nucl Inst Meth Phys Res B*, 282 (2012) 48.
39 Osendi M I & Moya J S, *J Am Ceram Soc*, 68 (1985) 135.
40 Benyagoub A, *Nucl Inst Meth Phys Res B*, 218 (2004) 451.
41 Stefanic G & Musić S, *Croat Chem Acta*, 69 (2014) 223.
42 Tsunekawa S, Asami K, Ito S, Yashima M & Sugimoto T, *Appl Surf Sci*, 252 (2005) 1651.
43 Kumar D, Singh A, Kaur M, Rana V & Kaur R, *AIP Conf Proc*, 1953 (2018) 030074.
44 Hwang S M, Choi J H, Lee S M, Lim J H & Joo J, *J Phys Chem C*, 116 (2012) 11386.
45 Kavitha A, Subaramanian N S & Vadivel S, *IOP Conf Ser: Mater Sci Eng*, 73 (2015) 012005.
46 Ratan A, Kunchakara S, Tripathi A & Singh V, *Polym Test*, 91 (2020) 106776.
47 Chauhan V, Gupta T, Singh P, Sahare P D, Koratkar N & Kumar R, *Phys Lett A*, 383 (2019) 898.
48 Keiteb A S, Saion E, Zakaria A & Soltani N, *J Nanomater*, (2016) 1913609.
49 Trejo-arroyo D L, Acosta K E, Cruz J C & Valenzuela-muñiz A M, *Appl Sci*, 9 (2019) 1.
50 Chintaparty C R, *Int J Light Electron Opt*, 127 (2016) 4889.
51 Domino M, Narkiewicz U & Witkowski B S, *Opt Mater*, 74 (2017) 16.
52 Sagaya N C, Manikandan A, Kennedy L J & Vijaya J J, *J Colloid Interface Sci*, 389 (2013) 91.
53 Clarke D R, Oechsner M & Padture N P, *MRS Bulletin*, 37 (2012) 891.
54 James S, Advanced ceramics for dentistry (Elsevier 1st Edn) 2013. ISBN 978-0123946195.
55 Yao J H, Elder K R, Guo H & Grant M, *Phys Rev B*, 47 (1993) 14110.
56 Kumari L, Du G H , Li W Z, Vennila R S, Saxena S K & Wang D Z, *Ceram Int*, 35 (2009) 2401.
57 Omidi S, Negahdary M & Aghababa H, *Electron J Biotechnol*, 11 (2015) 46.
58 Rothenstein D, *Cryst Eng Commun*, 17 (2015) 1783.
59 Waghmare M A, Pawar K S, Pathan H M & Ubale A U, *Mater Sci Semicond Process*, 72 (2017) 122.
60 Liu X, Pappas I, Fitzgerald M, Zhu Y, Eibling M & Pan L, *Mater Lett*, 64 (2010) 1591.
61 Wang Z, Lu Y, Yuan S, Shi L, Zhao Y, Zhang M & Deng W, *J Colloid Interface Sci*, 396 (2013) 9.
62 Thaveedeetrakul A, Witit-Anun N & Boonamnuayvitaya V, *Appl Surf Sci*, 258 (2012) 2612.
63 Balakrishnan G, Thanigaiarul K, Sudhakara P & Song J, *Appl Phys A*, 110 (2013) 427.

64 Andrieux M, Ribot P, Gasquères C, Servet B & Garry G, *Appl Surf Sci*, 263 (2012) 284.
65 Ali N, Bashir M, Batool S, Riaz S & Naseem S, *Mater Today*, 2 (2015) 5771.
66 Heshmatpour F & Aghakhanpour R B, *Powder Technol*, 205 (2011) 193.
67 Harris D C, *Infrared Phys Technol*, 39 (1998) 185.
68 Zhao S, Ma F, Xu K W & Liang H F, *J Alloys Compd*, 453 (2008) 453.
69 Zalnezhad E, Hamouda A M S, Jaworski J & Kim Y D, *Nat Publ Sci Rep*, 6 (2016) 33282.
70 Harris D C, Infrared Windows and Dome Materials, SPIE Optical Engineering Press, Bellingham, WA, Tutorial 10 (1992),
71 Vagkopoulou T, Koutayas S O, Koidis P, Strub J R, *Eur J Esthet Dent*, 4 (2009) 130.
72 Bona A D, Pecho O E & Alessandretti R, *Materials*, 8 (2015) 4978.
73 Venkataraj S, Kappertz O, Weis H, Drese R, Jayavel R & Wuttig M, *J Appl Phys*, 92 (2002) 3599.
74 Xiao D, He G, Sun Z, LvJ, Jin P, Zheng C & Liu M, *Ceram Int*, 42 (2015) 759.
75 Kumari L & Li WZ, *Cryst Growth Des*, 9 (2009) 3875.
76 Liang J, Deng Z, Jiang X, Li F & Li Y, *Inorg Chem*, 41 (2002) 3602.
77 Nagabhushana K R & Singh F, *Opt Mater (Amst)*, 107 (2020) 109984.
78 Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E & Russo R, *Science*, 292 (2001) 1897.
79 Blasse G & Grabmaier B C, Luminescent Materials; Springer: Heidelberg, (Spriner 1st Edn.) 1994.
80 Wang J, Zhao L, Luu N H, Wang D & Nakashima H, *Appl Phys A*, 80 (2005) 1781.
81 Nesamani I F P, Prabha V L, Paul A & Nirmal D, *Adv Condens Matter Phys*, (2014) 828492.
82 Chintaparty C R, *Int J Light Electron Opt*, 127 (2016) 4889.
83 Choi Y & Song C K, *Org Electron*, 52 (2018) 195.
84 Kumar K R, Pridhar T & Balaji V S S, *J Alloys Compd*, 765 (2018) 171.
85 Hannink R H J, Murray M J & Scott H G, *Wear*, 100 (1984) 355.
86 Shimizu K, Oka M, Kumar P, Kotoura Y, Makinouchi T Y K & Nakamura T, *J Biomed Mater Res*, 27 (1993) 729.
87 Christel P, Meunier A & Heller M, *J Biomed Mater Res*, 23 (1989) 45.
88 Vasylkiv O & Sakka Y, *J Am Ceram Soc*, 86 (2003) 299.
89 Sakka Y, Suzuki T S, Morita K, Nakano K & Hiraga K, *Scripta Mater*, 44 (2001) 2075.
90 Singaravel A, Nathan C, Tah R & Balasubramanium M K, *J Oral Biol Craniofacial Res*, 8 (2017) 221.
91 Piva R H & Piva ***D H,*** *Mater Res*, 19 (2016) 31.
92 Jones RL, Reidy RF & Vanadate M D, *J Am Ceram Soc*, 76 (1993) 2660.
93 Tanaka H, Maeda T, Narikiyo H & Morimoto T, *J Asian Ceram Soc*, 7 (2019) 460.
94 Nawa M, Nakamoto S & Sekino T, *Ceram Int*, 24 (1998) 497.
95 Denti L, *Int J Appl Eng Res*, 12 (2017) 1452.
96 Emrullahoglu A C B & Yazici E G, *J Sci*, 3 (2014) 177.
97 Rane A V, K Kanny, Abitha V K & Thomas S, Mater Sci, (2018) 121.
98 Nunes D, Pimentel A, Santos L, Barquinha P, Pereira L, Fortunato E & Martins R, Metal Oxide Nanostructures: Synthesis, Properties and Applications, (Elsevier 1stEdn.), 2018.
99 Alaei M, Rashidi A & Bakhtiari I, *Iran J Chem Chem Eng*, 33 (2014) 47.
100 Rossignol S, Madier Y & Duprez D, *Catal Today*, 50 (1999) 261.
101 Arsent'ev M Y, Kalinina M V, Tikhonov P A, Morozova L V, Kovalenko A S, Koval'ko N Y, Khlamov I I & Shilova O A, *Glass Phys Chem*, 40 (2014) 362.
102 Kumar P R & MuthuChudarkodi R R, *Int J Sci Eng Manag Res*, 2 (2017) 2456.
103 Nikam AV, Prasad B L V & Kulkarni A A, *Cryst Eng Commun*, 20 (2018) 5091.
104 Gupta D & Katoch A, Applications of Nanocomposite Materials in Drug Delivery, (Elsevier 1stEdn.) 2018.
105 Manjunatha S & Dharmaprakash M S, *J Lumin*, 180 (2016) 20.
106 Hembram K P S S & Rao G M, *J Nanosci Nanotechnol*, 8 (2008) 4159.
107 Tiwari A, Rawlins J & Hihara L H, Intelligent Coatings for Corrosion Control, (Elsevier 1stEdn.) 2014.
108 Brinker C F & Scherer G W, Academic Press, Inc, San Diego, USA, 1990.
109 Tack B, Cho J, Hee K, Min K, Shin K & Sung D, *Org Electron*, 28 (2016) 1.
110 Kumar S, Bhunia & Ojha A K, *Phys E: Low Dimens Syst Nanostruct*, 66 (2015) 74.
111 Alotaibi A M & Mahfouz R, *Mater Res*, 15 (2012) 986.
112 Buschow K H L, Encyclopedia of Materials: Science and Technology, (Elsevier 1st Edn) 2001.
113 Ouyang W, SantiagoA R P, Cerdán-Gómez K, Luque R, *Photoact Inorg Nanopart*, (2019) 109.
114 Modeshia D R & Walton R I, *Chem Soc Rev*, 39 (2010) 4303.
115 Shaik M R, Alam M, Adil S F, Kuniyil M, Al-warthan A, Siddiqui M R H, Tahir M N, Labis J P & Khan M, *Materials*, 12 (2019) 711.
116 Santos M S, Freitas J C C & Dalmaschio C J, *Cryst Eng Comm*, 22 (2020) 1802.
117 Keukeleere K D, Roo J D, Lommens P, Martins J C, Van Der Voort P & Driessche I V, *Inorg Chem*, 54 (2015) 3469.
118 Kulkarni S K, Synthesis of Nanomaterials — I (Physical Methods), Nanotechnology: Principles and Practices, (Spriner 3rd Edn) 2015.
119 Venkataraj S, Kappertz O, Weis H, Drese R, Jayavel R & Wuttig M, *J Appl Phys*, 92 (2009) 3599.
120 LiN C C, Chang Y P & Lin H B, *Nanoscale Res Lett*, 7 (2012) 187.
121 Prabakar K, Park A, Cho N, Lee W L, Hwangbo C K, Lee J G & Lee C, *Vacuum*, 82 (2008) 1367.
122 Dhand C, Dwivedi N, Loh J & Jie N, *RSC Adv*, 5 (2015) 105003.
123 Balakrishnan G, Kuppusami P, Sastikumar D & Song J, *Nanoscale Res Lett*, 8 (2013) 1.
124 Mittra J, Abraham G J, Kesaria M, Bahl S, Viswanadham C S, Kulkarni U D & Dey G K, *Mater Sci Forum*,710 (2012) 757.
125 Al-Kuhaili M F & Durrani S M A, *J Alloys Compd*, 509 (2011) 9536.

126 Gottmann J & Kreutz E W, *Surf Coatings Technol*, 116 (1999) 1189.
127 Martin P J & Bendavid A, *Thin Solid Films*, 518 (2010) 5078.
128 Zhao Z W, BK Tay, Yu G Q & Lau S P, *J Phys Condens Matter*, 15 (2003) 7707.
129 Yu G Q, Tay B K & Zhao Z W, *Appl Phys A*, 81 (2005) 405.
130 Sharma J, Singh R, Kumar A, Singh T, Agrawal P & Thakur A, *Appl Nano Sci*, 8 (2018) 359.
131 Ahmed H A, Abu-Eishah S I, Ayesh A I & Mahmoud S T, *J Phys: Conf Ser*, 869 (2017) 012027.
132 Kwaśny J & Balcerzak W, *Tech Trans*, 114 (2017) 105.
133 Mattinen M, Manner T, Lindstro H, Seppa H, Popov G, Bac G, Kemell M, Jalkanen P, Mizohata K, Suihkonen S, Vehkama M, BarryT, Ritala M, Leskela M & Koivula H M, *Chem Mater*, 32 (2020) 8216.
134 Johnson R W, Hultqvist A & Bent S F, *Biochem Pharmacol*, 17 (2014) 236.
135 Wang X, Ghosh S K, Afshar-mohajer M, Zhou H, Liu Y, Han X, Cai J, Zou M & Meng X, *J Mater Res*, 35 (2019) 804.
136 Casta H, Duefias S, Garcia H, Gomez A, Bailon L, Kukli K, Niinisto J & Ritala M, *Proc Spanish Conf Electron Dev*, (2009) 8.
137 Kukli K, Kemell M, Köykkä J, Mizohata K, Vehkamäki M, Ritala M & Leskelä M, *Thin Solid Films*, 589 (2015) 597.
138 Nice K, Strickland J, How Fuel Cells Work: Polymer Exchange Membrane Fuel Cells. (2011), https://auto.howstuffworks.com/fuel-efficiency/alternative-fuels/fuel-cell.htm.
139 Iannaci A, Mecheri B, Epifanio A D & Licoccia S*, Int J Hydrogen Energy*, 39 (2014) 11241.
140 Elshazly E S & Abdelal O A A, *Int J Miner Metal Mater*, 1 (2012) 130.
141 Cebollero J A, Lahoz R, Laguna-Bercero M A, Peña J I, Larrea A & Orera V M, *Int J Hydrog Energy*, 42 (2017) 13939.
142 Wilk G D, Wallace R M & Anthony J M, *J Appl Phys*, 89 (2001) 5243.
143 Sobczynska D & Torbicz W, *Sens Actuators B Chem*, 6 (1984) 93.
144 Pešic M, Knebel S, Geyer M, Schmelzer S, Böttger U, Kolomiiets N, Afanas'ev V V, Cho K, Jung C, Chang J, Lim H, Mikolajick T & Schroeder U, *J Appl Phys*, 119 (2016) 64101.
145 Zhitomirsky I & Petric A, *Mater Lett*, 50 (2001) 189.
146 Gao P, Meng L J, Santos M P, Teixeira V & Andritschky M, *Appl Surf Sci*, 173 (2001) 84.
147 Ma C Y, Lapostolle F, Briois P & Zhang Q Y, *Appl Surf Sci*, 253 (2007) 8718.
148 Prabakar K, Park A, Cho N, Lee W I, Hwangbo C K, Lee J G & Lee C, *Vacuum*, 82 (2008) 1367.
149 Dondapati H, Ha D, Jenrette E, Xiao B & Pradhan A K, *Appl Phys Lett*, 105 (2014) 052105.
150 Voss C, Subramanian S & Chang C H, *J Appl Phys*, 96 (2004) 5819.
151 Lee J S, Chang S, Koo S M & Lee S Y, *IEEE Electron Dev Lett*, 31 (2010) 225.
152 Rao A, Chaurasia P & Singh B R, *Radiat Effect Defects Solids*, 171 (2016) 187.
153 Brunet M, Kotb H M, Bouscayrol L, Scheid E, Andrieux M, Legros C & Schamm-Chardon S, *Thin Solid Films*, 519 (2011) 5638.
154 Wu Y H, Lin C C, Chen L L, Hu Y C, Wu J R & Wu M L, *Appl Phys Lett*, 98 (2011) 013506.
155 Lee H, Choi S, Cho K & Kim S, *Thin Solid Films*, 516 (2007) 412.
156 Panda D & Tseng T, *Thin Solid Films*, 531 (2013) 1.
157 Helmer J D & Driskell T D, Research on Bioceramics Symp South Carolina (USA) Clemson University, 1969.
158 Volpato C A M, AltoéGarbelottoL G D, M Frede L C & Bondioli F, *Adv Ceram*, 397 (2011) 420.
159 Chevalier J & Gremillard L, *Compr Zirconia Biomaterial*, (2011).
160 Ito A, Tateishi T, Niwa S & Tange S, *Clin Mater*, 12 (1993) 203.
161 Chevalier A, *Biomaterials*, 27 (2006) 535.
162 Hassan M F & Megahed S M, Current Advances in Mechanical Design and Production VII, (Elsevier 1st Edn) 2000.
163 Yau T L & Annamalai V E, Corrosion of Zirconium and its Alloys, (Elsevier), 2016. doi:10.1016/B978-0-12-803581-8.01641-6.
164 Stoller R & Konings R J M, Comprehensive Nuclear Materials (Elsevier 2ndEdn), 2012.