Effect of Solvents on the Morphological and Optical Properties of SiO_2 Film Prepared by Sol-Gel Method

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Abstract

The present work deals with the synthesis and characterization of SiO_2 by sol-gel method and also provide a basic understanding of the effect of solvents on the growth of SiO_2 .The precursor solutions were made by mixing tetraethoxysilicate (TEOS), acetone, ethanol and deionized water. The results show that the obtained SiO_2 particles were composed of spherical nanoparticles. In this work, we deals with different solvents, which are helpful for the enhancement of optical properties and surface morphologies. Growth rate of SiO_2 can be observed through scanning electron microscopy (SEM) and optical properties can be examined by using the UV-Visible spectroscopy. SEM and UV-Visible analysis revealed that all the required morphologies and absorption spectra were observed which were indicative of the successful synthesis of silica particles. The solvents suppress the growth of SiO_2 films, the observed spectra of samples in the ultraviolet region.

Keywords: *SiO_2, thin films, sol-gel method, characterization*

Introduction

Nanocrystalline semiconductor metal oxides have achieved a great importance in our industrial world today. They may be defined as metal oxides with crystal size between 1 and 100 nm. Particles smaller than tens of nanometers in primary particle diameter (nanoparticles) are of interest for the synthesis of new materials because of their low melting point, special optical properties, high catalytic activity, and unusual mechanical properties compared with their bulk material counterpart [1].Many methods have been developed to control the size of nanoparticles such as Langmuir–Blodgett films [2], vesicles [3], and reverse micro-emulsions [4].The chemical and physical properties exhibited by these materials depend, among others, on both the composition and the degree of homogeneity. Therefore, different synthesis strategies have been developed such as coprecipitation, flame hydrolysis, impregnation, chemical vapor deposition, etc. [5-6]. Sol-gel technology has drawn increased attention in recent years for the fabrication of various electric/photonic materials in various configurations, such as monoliths, coatings, fibers and films for optical device applications [7-11]. The precursor solution generally consists of a metal oxide dissolved in some solvent oxygen for oxide formation of the metal. The metal salts undergo hydrolysis and polycondensation reactions to form a gel-like colloidal suspension consisting of both a liquid and a solid phase whose morphologies range from discrete particles to continuous polymer networks. The solid phase consists of the metal oxide and the liquid phase consists of the solvent. Sol-gel techniques has unique advantages such as low temperature processing, high homogeneity of final products and its capability to generate materials with controlled surface properties and pore structures [12, 13]. Oxides prepared via this technique exhibit high surface area and have potential for applications such as sorbents, catalysts and electrodes.

SiO_2 nanosize particles have attracted significant interest of materials scientists and physicists due to their special properties and have attained a great importance in several technological applications such as photo-catalysis, sensors, solar cells and memory devices. SiO_2 has been a subject of intensive research due to its outstanding physical and chemical characteristics. During last decade, basic and applied research focused on the preparation and characterization of SiO_2 thin films [14], which feature large energy gap, excellent visible and near-IR transmittance, high refractive index and dielectric constant. When silica has synthesized $Ag@SiO_2$ nanoparticle with a core-shell structure the optical properties in plasmon resonance peak [15], also silica prepared by spray drying shows the SiO_2 nanoparticles aggregate to SiO_2 microspheres [16]. When polyimide/silica composite film synthesized by sol-gel with water and solvents give thermal stability investigated thermogravimetric analysis [17]. Here, we prepared silica film by sol-gel process by successfully investigated the properties which applicable in the several fields. In this work, we report novel sol-gel method to synthesis SiO_2 film at room temperature and the film were analyzed for surface morphology by SEM and SiO_2 nanoparticle absorption spectra by UV-Visible spectroscopy.

Experimental

All reagents used were of analytical grade purity and were procured from Merck Chemical Reagent Co. Ltd. India. In this synthesis procedure, we use TEOS (tetraethoxysilicate) as a precursor material with addition of surfactant dimethyl-formamide (dmf), catalysts hydrochloric-acid (HCl) and different solvents such as acetone, ethanol and deionized water.

Synthesis of Silica Oxide Nanoparticles

In the synthesis of SiO_2 particles, tetraethoxysilicate (TEOS) (2.5 ml), dimethyl-formamide (2.5 ml) prepared by dissolving in either acetone, ethanol, or deionized water (15 ml) mixture was stirred for 10 min, and added catalyst HCl drop wise to the above mixture and stirred magnetically 30 min at room temperature and become a transparent homogeneous solution. Now the prepared sample is kept for aging about 24 hours for gel preparation. The gel is again kept for long time about 15 days for dry. This SiO_2 solution was further used to produce different form of SiO_2 powder and thin film. The film was formed by dipping well cleaned glass substrates into the sol at room temperature and carried out in air at room temperature. Finally, film was heated at 110^{o}C for 4 hours and cool at room temperature.

Characterization

The prepared silica nanoparticles were characterized for surface morphology was studied by using SEM (JEOL- JSM-6390) and for optical properties was studied by UV–Vis diffuse absorption spectra were recorded with a Carry 5000 UV-Vis spectroscopy.

Result and Discussion

Scanning Electron Microscopy

We used SEM to study the morphology of the samples prepared by using different solvents. SEM spectra are useful tools to follow the observation i.e. structural changes that occur at the surface and in the silica film obtained via sol-gel process. A major concern in the production of monolithic dried gels is the prevention of cracks during aging and drying steps. Fig. 1(a) shows that sol of acetone converted into gel and then in crystalline form immediately with crackles surface. And, SiO_2 film calcined at 110^{o}C for 4 hours are shown rods of diameter 350 nm. Fig. 1(b) represents the fine structures of silica film which is obtained by the ethanol. Here we observed that some crack on the surface or a fine structure be obtained since these samples takes more time to form the gel. SEM images of SiO_2 film are shown a formation of rods. Fig. 1(c) represent spherical size of silica film structure which contain deionized water and take much more time to form a gel, and shows some more cracks as compared to the sample containing ethanol.

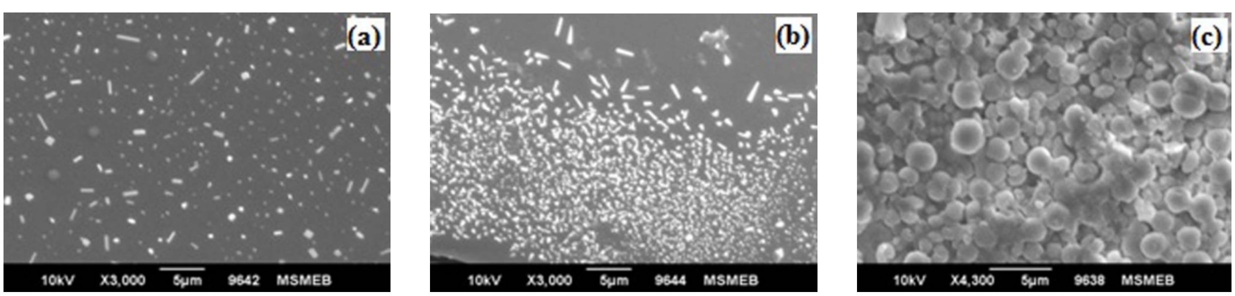

Figure 1 SEM analysis of SiO_2 thin film (a) with acetone, (b) with ethanol, and (c) with water

The sample obtained from deionized water, more internal silanol groups are retained in the silica network. Hence, due to this silanols more stresses developed which causes cracks and irregularities on the silica layer as compared to ethanol and acetone which can be observed on their SEM images for film samples. An approach to overcome this destructive phenomenon consists of the use of acetone. For samples obtained with acetone, OH group is removed more easily and less internal silanols remain in the samples and a better results observed which can also shown in the SEM images. Hence, during the experimental results we conclude that acetone; have been found to reduce cracking, which helps to convert the wet gel into a monolithic xerogel within a reasonable time and have rods. Same phenomena occur as by using ethanol it takes long aging time to form gel as compared to silica gel with acetone, and by using deionized water it takes more long time to form gel as compared to ethanol. SEM observation of silica with water shows that the obtained product exclusively consisted of spherical nanoparticles.

UV-Visible Spectroscopy

Absorption spectra were acquired on an UV-Vis spectrophotometer. The UV-Visible spectroscopy used to obtain optical behavior of the SiO_2 films observed the absorption spectra as shown in Fig. 2. The resultant graphs are analyses in absorption vs. wavelength. A graph shows drastically variations in peak values at same excitation wavelength of different solvents acetone, ethanol and deionized water.

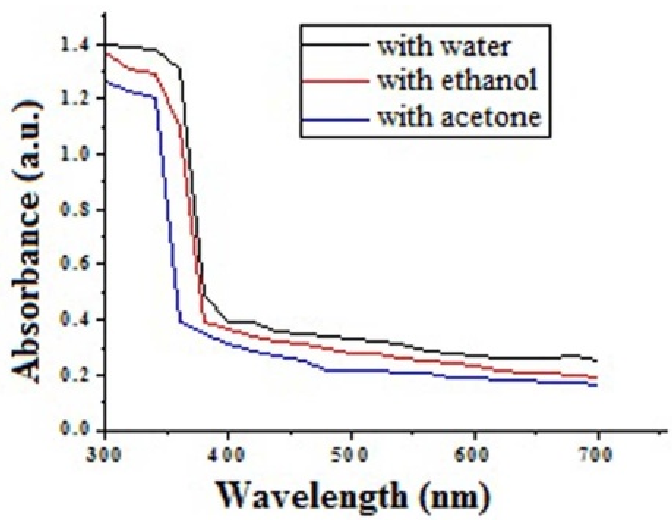

Figure 2 UV-Vis spectra of SiO_2 thin film (a) with acetone, (b) with ethanol, and (c) with water

The optical properties of SiO_2 nanoparticle in ethanol as a solvent are normally exhibits two emission peaks which are due to the oxygen vacancy. One of the impressive features of semiconductor nanoparticle is their ability to emit light upon excitation with shorter wavelength of equivalent to the absorption onset, an electron is promoted from valence band to the conduction band, and on relaxation a photon is emitted. The wavelength maximum emission from the absorption peak and this is a typical feature of well-passivity nanoparticle. The absorption spectrum of SiO_2 nanoparticles prepared in acetone. The exciton peak appears compared to the bulk, due to the particles nano-size regime exhibiting quantum confinement effect. The large particle size and shape of the particles synthesized in water as a solvent influenced the appearance of the absorption peak. The absorption peak for water is also much more tailing compared to the peak of acetone and ethanol. The absorption spectrum of SiO2 with water consists of a single broad intense absorption around 391 nm, compared SiO2 with acetone showed absorbance in the shorter wavelength region than ethanol showed a blue shift in the absorption spectra. The band gap of the samples was determined by the equation [1].

$$E_g = 1239.8/\lambda \qquad (1)$$

Where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edge in the spectrum. UV-Visible spectroscopy results showing synthesized material's absorbance in UV region. Due to this it can be said that material's band-gap is 3.17084 eV for water sample, 3.26263 eV for ethanol sample and 3.44389 eV for acetone sample. There are some other peaks which may be due impurities or presence of bi-products formed during synthesis. The blue shift in absorption edge in ethanol and acetone may be attributed due to the presence of chloride (Cl^-) ions which reduces the particle size, hence the shift on blue region is observed. Moreover, from all of the above UV-Visible spectra, it is clear that the samples prepared absorb in the UV region.

Conclusion

The sol-gel method can be used effectively for the synthesis of silica film. The SEM and UV-Visible analyses prove the successful synthesis of the desired material. The SiO_2 homogeneous sol and film obtained which can be used for catalytic purposes and adsorption processes. Reaction in ethanol results have in the formation of rods which are of smaller sizes with respect to those formed in acetone as a solvent have rods under similar conditions. SiO_2 film form spherical structure to water as a solvent, with strongly interconnected bond between the molecules. The structure of silica gel obtained by the addition of acetone present smaller values of shrinkage and higher value of monolithicity than gels and films obtained with as shown in SEM images. An optical behavior studied by the UV-Visible spectra of silica with water represents the highly intensive form or very high peak than ethanol to acetone. The absorption spectra of silica samples shows in the ultraviolet region.

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