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ARTICLE

Enhanced Visible Light Adsorption of Heavily Nitrogen Doped CeO_2 Thin Film via Ion Beam Assisted Deposition

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Abstract: CeO_2 is a promising material for the utilization of solar light in photocatalytic reactions. However, the major obstacle for these studies is the lack of reliable methods to incorporate the desired elements such as nitrogen into the crystal lattice of CeO_2. In the present study, a nitrogen-doped CeO_2 thin film was synthesized by IBAD technique. With this technique, the nitrogen was heavily and uniformly doped into the CeO_2 thin films. XPS analysis clearly demonstrates the greatest N concentration of 25 mol% can be doped in CeO_2 thin films which is much higher than that obtained via traditional methods. The high resolution N 1s spectrum shows that nitrogen dopants are uniformly doped into CeO_2 lattice by substituting O. The XRD results indicate ion bombardment on the growing film surface does not alter the crystal structure of the film by itself. Instead, the heavy nitrogen doping induces smaller grain size of CeO_2. The SEM images show that with the increase of N doping, the surface become smoother with smaller particle size. The heavily nitrogen doping also induces a red shift of the visible light absorbance from 380 nm to 450 nm.

Key words: CeO_2; nitrogen doping; ion beam assisted deposition; visible light absorbance

Metal oxides have been extensively studied for the utilization of solar light as energy source because of their relatively low cost, high photostability and useful optoelectronic properties[1-4]. However, their photocatalytic capabilities are limited to ultraviolet (UV) illumination, which means that only a small portion (3%~4%) of the whole solar spectrum can be utilized. Therefore, it is greatly interesting to develop photocatalysts that can yield high reactivity under visible light that accounts for around 45% of solar spectrum.

Since the report of nitrogen-doped TiO_2 by Asahi et al.[5], N-doping has been demonstrated to be an important method for modifying the properties of oxides, which show good mechanical, catalytic and optical properties[6-11]. Cheng et al[12] reported the nitrogen doping into ZrO_2 increased the anion vacancy concentration and stabilized the cubic or tetragonal form at room temperature, which has been reported as super-ionic conductors. Stoichiometric oxynitrides also have useful optical properties such as photocatalytic TaON and yellow-red pigments in the solid solution series $CaTaO_2N$-$LaTaON_2$[13,14].

As one of the most abundant and least expensive rare earth metal oxides, cerium oxide has been extensively studied as catalyst[15], electrolyte materials of solid oxide fuel cells[16], UV shielding materials[17], and chemical mechanical planarization materials[18] because of its specific physical and chemical properties. Bamwenda et al. have reported that cerium dioxide is a promising material for the utilization of solar light in photocatalytic reactions[19]. Mao et al[20] have recently reported photocatalytic activity under visible light of nanoparticles of nitrogen-doped ceria in methylene blue decomposition. However, the major obstacle for the studies on the nitrogen doping is the lack of reliable methods to incorporate the desired elements. For

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example, Jorge et al [21] showed that just 4.5 mol% N can be introduced into ceria under reducing conditions between 550 and 900 °C through ammonolysis.

In this study, we synthesized nitrogen-doped CeO_2 thin films by IBAD technique. The morphology and crystal structure of these thin films were characterized by SEM and XRD techniques. The chemical states of nitrogen in the CeO_2 were investigated by X-ray photoelectron spectroscopy (XPS).

1 Experiment

1.1 Thin Film Fabrication

The ion-beam-assisted deposition (IBAD) system used in this study consisted of a 3 kW electron-beam evaporator, 3-cm-diameter Kaufman-type ion source, and a substrate holder with a heater made of tantalum. A quartz-crystal monitor was used to control the film thickness as well as the deposition rate. The material of substrate was microscope glass slide, which was ultrasonically cleaned in acetone and methanol baths successively, and blow dried under nitrogen purge. Prior to deposition, the substrate was cleaned by 1000 eV Ar^+ ions for 5 min to remove surface contamination. Nitrogen-doped cerium oxide was deposited by electron-beam evaporation of cerium oxide, anatase, 99.9% (Alfa Aesar, USA). Simultaneously, the growing CeO_2 film was bombarded by nitrogen ions. During deposition, the nitrogen partial pressure was controlled at a stable value in the range of 1.3×10^{-2}~3.9×10^{-2} Pa. The working pressure and the deposition rate were adjusted to regulate N incorporation. The deposition was carried out at a substrate temperature of 450 °C. After the deposition, the thin film was heated to about 150 °C and then bombarded by ions (nitrogen 50% and oxygen 50%) for 3 min followed by holding at 80 °C for 20 min in oxygen atmosphere.

1.2 Characterization

The crystal structures of these films were analyzed by the glancing angle X-ray diffraction (GAXRD) using a D/MAX-2004 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Ni-filtered Cu (λ = 0.15418 nm) radiation at 56 kV and 182 mA. The morphology of these films was examined by scanning electron microscopy (SEM). SEM observation was made with a SEM LEO SUPRA 35 (Carl ZEISS Inc., Oberkochen, Germany) at an acceleration voltage of 20 kV. Before imaging, the samples were sputtered with gold for 120 s to enhance their surface conductivity (Cress ington Sputter Coater 208HR, Cressington Scientific Instrument Ltd., Watford, U. K.). The UV-vis spectra of these films were measured on a UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). Compositions of these samples were analyzed by a X-ray photoelectron spectrometer (XPS). The XPS measurements were made using an ESCALAB250 X-ray Photoelectron Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA) with an Al K anode (1486.6 eV photon energy, 300 W).

2 Results and Discussion

2.1 Surface elemental composition and chemical states of N doped CeO_2

XPS spectra were obtained for each sample and analyzed to provide compositional data, as shown in Table 1. XPS results clearly demonstrate the existing elements of Ce 3d, O 1s and N 1s. The composition of the film was estimated by taking the average intensity ratio from multiplex scans of Ce 3d, O 1s and N 1s using the method adopted previously[21]. Since the evaporation and ion bombardment were simultaneous and well controlled in the deposition process, compositional ratios as-obtained from a limited volume of the film were taken to represent the whole film. A substantial increase in nitrogen concentration is observed with $CeO_{1.94}N_{0.01}$, $CeO_{1.76}N_{0.17}$ and $CeO_{1.64}N_{0.25}$, responding to the molar ratio of N/Ce of 1%, 17% and 25%, respectively. The N concentration is much higher than molar ratio of 4% in the Ref.[22].

The X-ray photoelectron spectroscopy was used to study the surface chemical compositions of the N doped ceria. As shown in Fig.1, the full scale XPS spectra reveal the presence of Ce, O and adsorbed C. After N is doped into ceria, the N 1s spectra occur in the XPS wide scan, which confirm the presence of N. High resolution XPS measurements were performed on $CeO_{1.64}N_{0.25}$. From the experimental N 1s line shape, two contributions are identified with binding energies of 400.1 and 396.1 eV. The 400.1 eV contribution correspond to molecularly chemisorbed nitrogen (γ-N_2) at the surface [22], while the 396.1 eV contribution is assigned to the formation of Ce-N bonds, which indicates that N is successfully incorporated into CeO_2.

2.2 Crystal structure and surface morphology analysis

Fig.2 shows some representative X-ray diffraction patterns of the specimens at various N doping levels. The diffraction peaks of both pure CeO_2 and N doped CeO_2 are indexed to the fluorite cubic phase of ceria with the lattice constant a=0.5411 nm, which are in good agreement with the JCPDS card No.43-1002, whereas samples with higher nitrogen doping concentration show a wide (111) peak.

Table 1 Composition data and band gap (E_g) for N doped CeO_2

N_2 partial pressure/$\times10^{-2}$Pa	x	(N+O)/Ce	E_g/eV	Sample
0	0	1.96	3.35	$CeO_{1.96}$
1.3	0.01	1.95	3.30	$CeO_{1.94}N_{0.01}$
2.6	0.17	1.93	2.62	$CeO_{1.76}N_{0.17}$
3.9	0.25	1.89	2.14	$CeO_{1.64}N_{0.25}$

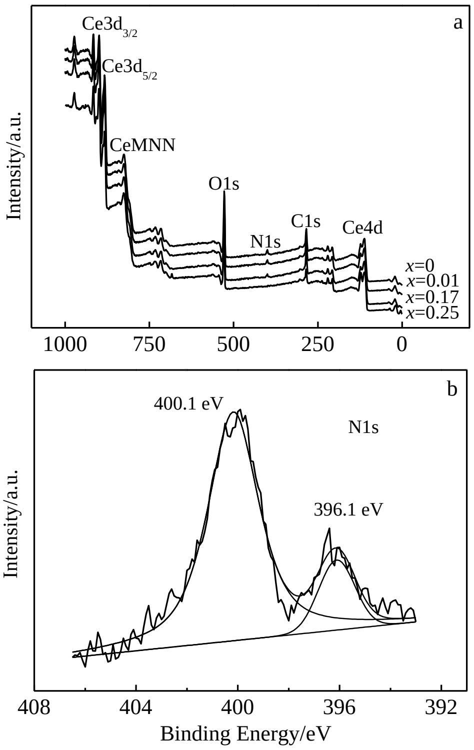

Fig.1 XPS spectra of the surface chemical compositions of the N doped ceria: (a) the full scale XPS spectra of CeON with different N-doping levels and (b) XPS high-resolution scans over the N 1s peak of $CeO_{1.64}N_{0.25}$ sample

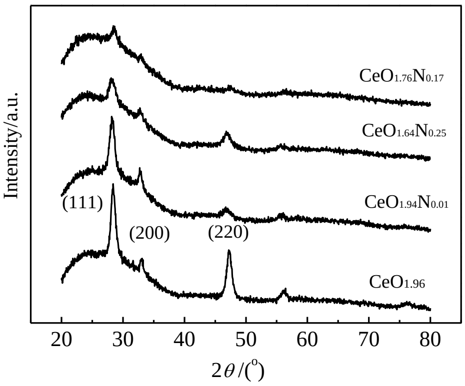

Fig.2 XRD patterns of the pure and N doped CeO

Apparently, ion bombardment on the growing film surface does not alter the crystal structure of the film by itself. Instead, the heavy nitrogen doping induces smaller grain size of CeO_2, which is also observed in the SEM images of the pure CeO_2 and CeON thin film, as shown in Fig.3.

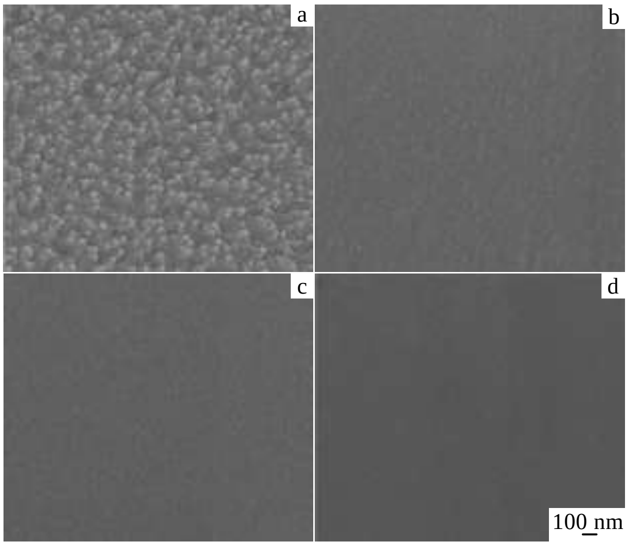

Fig.3 SEM images of pure CeO_2 (a) and CeON thin film surfaces: (b) $CeO_{1.94}N_{0.01}$, (c) $CeO_{1.76}N_{0.17}$, and (d) $CeO_{1.64}N_{0.25}$

From Fig.3a we can see that the pure ceria shows a triangular pyramidal shape. After N doping, the triangular pyramids become smaller or disappear compared with pure CeO_2, as seen in Fig.3b. Furthermore, with the increase of N doping, the surface becomes smooth with smaller particle size, as shown in Fig.3c-3d, which is corresponded with the XRD results.

2.3 Optical properties analysis

Fig.4 shows the optical property of all the thin films, investigated by measuring the optical absorbance spectrum using UV-Vis spectrophotometer in the transmission mode. The pure CeO_2 thin film exhibits its characteristic spectrum with the major absorbance in the UV range, whereas the CeON, synthesized by IBAD doping method presents a clear shift into the visible-light range (wavelength > 400 nm). we also observe that with the increase of N-doping levels, the absorption of N-doped CeO_2 experiences a red shift. The greatest shift is observed in to 450 nm. The results indicate that the improved dopant concentration and uniform distribution of substitutional nitrogen increases visible light absorption in CeON thin film.

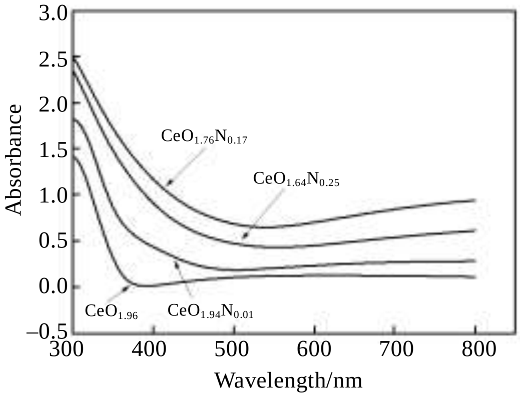

Fig.4 Optical absorbance (in arbitrary units) of CeON with different N-doping levels

3 Conclusions

1) The nitrogen doping CeO_2 thin films can bee synthesized by IBAD technique.

2) The 25 mol% nitrogen is introduced into CeO_2 thin films, which is much higher than that via traditional methods.

3) The high resolution N 1s spectrum shows that the nitrogen is uniformly doped in CeO_2 thin films by substituting O via IBAD.

4) The ion bombardment on the growing film surface does not alter the crystal structure of the film by itself. Instead, the heavy nitrogen doping induces smaller grain size of CeO_2.

5) With the increase of N doping, the surface become smoother with smaller particle size. The heavily nitrogen doping induces a red shift of the visible light absorbance from 380 nm to 450 nm.

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离子束辅助沉积法制备重掺 N 氧化铈提高其可见光吸收性能

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摘 要：氧化铈是一种潜在的可见光催化材料，但是如何实现在氧化铈晶格内的 N 掺杂是阻碍其发展的主要原因。采用离子束辅助沉积法制备了 N 掺杂的氧化铈薄膜材料，该方法实现了对氧化铈薄膜的高含量 N 掺杂，N 含量可高达 25%，远远高于采用传统方法制备的氮掺杂氧化铈。N 1s 的高分辨谱显示，掺杂的 N 替代了氧化铈中的 O 而实现了 N 在氧化铈晶格中的掺杂。XRD 结果显示，氧化铈薄膜在生长过程中，N 离子的轰击并没有改变氧化铈的晶体，但是改变了氧化铈薄膜表面形貌，从 SEM 上可以看出氧化铈表面颗粒变得细小，薄膜表面变得光滑。紫外可见吸收光谱显示，随着掺 N 量的增加，氧化铈的光吸收发生红移。

关键词：氧化铈；氮掺杂；离子束辅助沉积；光吸收

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