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ساخت لایه MoO_3 به وسیله‌ی بخار شعله برای کاربرد حسگر پلاسمونیکی گاز هیدروژن

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چکیده- امروزه، رنگزایی گازی اکسید فلزات واسطه برای حسگری اپتیکی گاز هیدروژن مورد توجه است. در این پژوهش، حسگری هیدروژن توسط فیلم‌های Pd/MoO_3 مورد بررسی قرار گرفته است. اکسید مولیبدن با استفاده از روش شعله در شرایط اتمسفر و در دمای اتاق بر روی زیرلایه‌ی شیشه لایه نشانی شده است. لایه‌های اکسیدی دارای فاز ساختاری β-MoO_3 می‌باشند. وقتی نمونه‌ی Pd/MoO_3 در دمای ۱۵۰ درجه سانتیگراد در معرض هیدروژن قرار می‌گیرد، رنگ آن به سمت آبی پر رنگ تغییر می‌کند. پس از هیدروژن دهی، تغییر فاز ساختاری در الگوی پراش پرتو ایکس مشاهده نمی‌شود. تصاویر FESEM ساختارهای وب مانند از تجمع ذرات کوچک (<10 nm) را نشان می‌دهد. به دلیل تشدید پلاسمون‌های سطحی پس از نفوذ هیدروژن، یک قله‌ی جذب اپتیکی پهن در ناحیه‌ی NIR ظاهرمی‌شود. باند جذب پلاسمونی اکسید مولیبدن با افزایش غلظت گاز هیدروژن علاوه بر افزایش شدت، به سمت طول موجهای کوتاهتر جابجا می‌شود. از این تغییرات طیفی می‌توان به عنوان ابزار حسگری گاز هیدروژن استفاده نمود.

کلید واژه- شعله، تری اکسید مولیبدن، پلاسمونیک، گاز هیدروژن، حسگر

Fabrication of MoO_3 Film by Flame Vapor Deposition for Plasmonic Hydrogen Gas Sensing Application

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Abstract- Nowadays, the gasochromic coloration of transition metal oxide has become more interesting for optical hydrogen sensing. This paper reports hydrogen sensing by Pd/MoO_3 films deposited on glass substrates by an atmospheric flame technique at substrates which were kept at room temperature. A β-MoO3 crystallite phase was detected for the flame deposited oxide layers. When Pd/MoO_3 films were exposed to hydrogen at 150 ° C, the sample's color changes to pale blue. After hydrogenation, no structural phase change is observed in the X-ray diffraction pattern. FESEM images shows a web like agglomeration of small particles (<10 nm). A broad LSPR absorption peak appeared in NIR region due to surface plasmon resonance after hydrogenation. The plasmonic absorption band of molybdenum oxide shifts to shorter wavelengths as the hydrogen gas concentration increases. This spectral variation of molybdenum oxide can be used as a plasmonic hydrogen gas sensor.

Keywords: Flame, MoO_3, Plasmonic, Hydrogen gas, Sensor

1. Introduction

Localized surface plasmon resonance (LSPR) is the mass oscillation of free electrons in nanoparticles smaller than the incident light wavelength[1]. Noble metals such as gold, silver and copper are the most common plasmonic nano materials in the visible and ultraviolet electromagnetic spectrum. While as, recently heavily doped semiconductors have been introduced as a new class of plasmonic materials whose plasmonic properties depend on the size, shape and concentration of the defects [2]. Unlike the noble metals, the properties of LSPR in semiconductors can be tuned by controlling carrier concentration by cation doping and introducing oxygen deficiency. One of the most promising of these plasmonic semiconductors is MoO_x nanoparticles with surface plasmon resonance at NIR region [3]. The plasmonic band in MoO_x is highly sensitive to hydrogen cation injection due to the formation of oxygen vacancy and quasi-metalic state. transition metal oxides such as WO_3 and MoO_3 exhibit plasmonic coloration properties in the presence of hydrogen gas [4], [5].

Todays, hydrogen is used as a clean and renewable energy source in many fields such as fuel cells, rockets and chemical industries [6]. However, using of hydrogen has many explosion risks. Therefore, it is crucial to develop a reliable and sensitive hydrogen sensor at all stages of production up to consumption units of hydrogen gas. Optical sensors have attracted much attention over other sensing techniques due to their simplicity, low cost, high sensitivity and low sparking probability and integration with integrated circuit systems [7].

Therefore, in this study, a thin layer of molybdenum trioxide and palladium was used for optical sensing of hydrogen gas. The MoO_3 layer is deposited on the glass by the solid fed flame vapor deposition. This method is very cheap, fast and simple. The Pd catalyst layer is then sputtered by the magnetron sputtering method on the oxide layer.

2. Experimental specification

Molybdenum oxide film synthesized by flame method using hydrogen and oxygen pre-mixed gas as fuel/oxidizer and a molybdenum plate (Mo) as a precursor which located 2 cm below the nozzle within the flame (Fig. 1). The glass substrates are in the flame direction at room temperature under atmospheric conditions. Molybdenum particles are separated from the rod and evaporated then combined with the hydrogen flame atmosphere containing oxygen gas and molybdenum oxide nanoparticles form and grow in the flame region and deposited on substrates. The flame deposition time was about 1 min. The palladium catalyst layer was then sputtered onto the Mo oxide layer for 3 seconds.

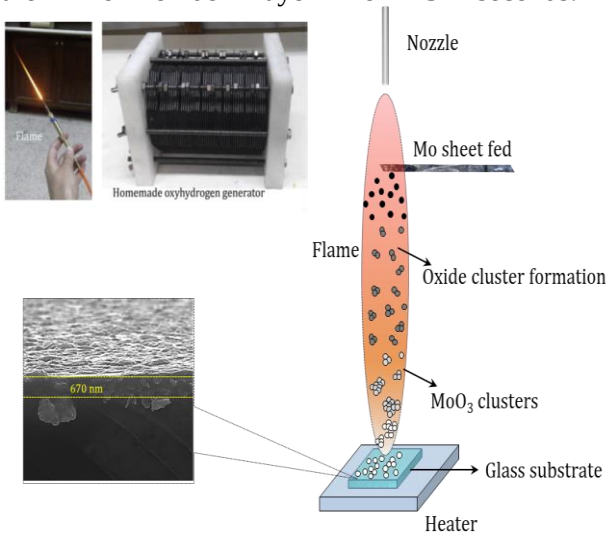

Fig.1: Schematic representation of oxyhydrogen generator and flame, flame synthesis of MoO_3 films and a cross-section FESEM image of produced films.

3. Results and discussion

3.1 Morphologies and structures characterizations

X-ray diffraction (XRD) was used to investigate the structural properties of the Pd/MoO_3 layer made by flame (Fig.2 (a)). The oxide thin layer diffraction pattern has sharp peaks that are compatible with the monoclinic β-MoO3 phase

(JCPDS card no. 47-1081). No additional peaks related to the Pd catalyst layer are observed, which might be due to its very small thickness (about 4 nm). To study the effect of hydrogen exposure process on films` crystalline structure, samples were exposed to H_2 10% for 2 min at 150 °C as operating temperate. Interaction with hydrogen gas also showed a gasochromic effect in which the samples were transformed from colourless to dark blue. The inset of Fig.2 demonstrates the photographic images of sample before and after hydrogen exposure.

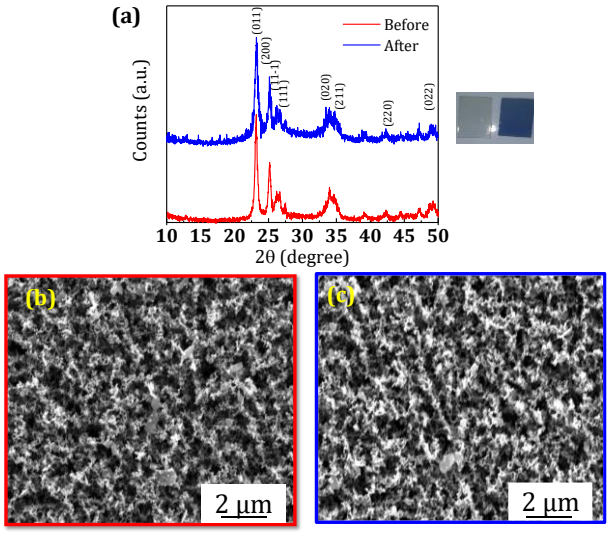

Fig.2: (a) XRD patterns of Pd/MoO_3 thin films before and after hydrogen exposure, the SEM images of thin films before (*b*) and after hydrogen exposure(*c*).

A comparison of the diffraction spectra shows that the crystal structure has not changed significantly due to hydrogenation. The non-significant phase change in the sample can be attributed to very fine NP's which provide a high effective surface area. After hydrogen intercalation and formation of localized H_2O and the high surface area allows them to remove easily from the surface at 150 °C operating temperature. As a result, the generated oxygen vacancies act as the colour centre and a stationary-phase gasochromic effect occurs.

The surface morphologies of the pristine and hydrogenated Pd/MoO_3 films are shown in Fig.2(b, c), respectively. The FESEM images of unexposed sample represent a highly porous web-like agglomeration of <10 nm NP's with numerous nanoplates crystallites of bigger size.

It is observed that hydrogenation of sample has no notable effect on the morphology as the overall feature of the web-like agglomerates is maintained.

3.2 Hydrogen sensing

Fig.3(a) illustrates the transmittance spectra of samples before and after 2 min injection of 0.1% hydrogen at 150 °C in a closed chamber. Before gas exposure, sample shows 70-95% transmission in the visible and NIR region, which are desirable initial optical transparency for an optical gas sensing device. With gas injection, the transmittance reduces remarkably to below 60% and at the same time, a broad absorption valley at 780 nm appears that is attributed to LSPR light absorption mechanism. The plasmonic band of the β-MoO_3 film lay in the shorter wavelength range than other gasochromic oxides which can be significant from the point of view of application [8].

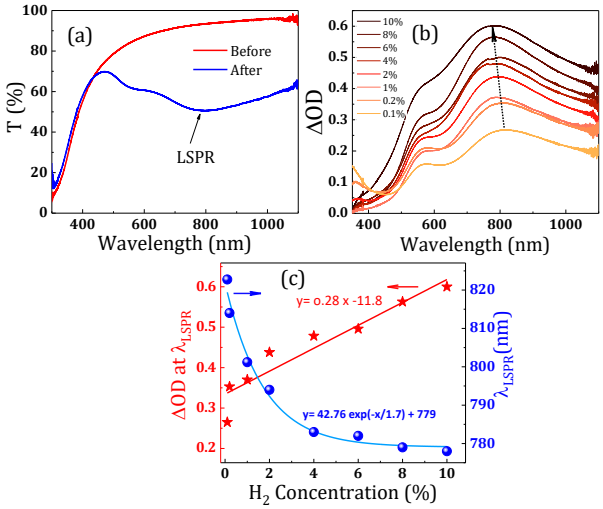

Fig.3: (a) Optical transmission spectra of before and after exposure 0.1% hydrogen exposure at 150 °C operating temperature (b) Typical LSPR optical ΔOD spectra of Pd/MoO_3 film at 0.1-10% hydrogen exposure and (c) ΔOD at λ_{max} and λ_{LSPR} as a function of hydrogen exposure

For a more detailed examination of the plasmonic mechanism in the samples, the pd/MoO_3 films

were exposed to different hydrogen concentrations in the 0.1-10% range, and the corresponding optical absorption spectra were recorded. Fig.3(b) demonstrate the corresponding optical density change (ΔOD, defined as $-log(T_{colored}/T_0)$) as the sensing platform. The Measurement errors of the data is based on the accuracy of the spectrophotometer device, ± 0.1 (nm) for the wavelength and ± 0.001 (%) for the optical transmittance. From the spectra set, the hydrogenated states present the broad LSPR band cantered at 780-825 nm depending on the gas concentration. This graph shows two main spectral variations within the hydrogenation process as depicted in part (c); increasing the absorption intensity and more importantly, a well-defined blue shift of the LSPR peak. The LSPR intensity exhibits a good linearity with gas concentration behaviour in the 0.2-10% range. On the other hand, about 35 nm blue shift is observed when gas concentration increases from 0.1-4% (below the hydrogen explosion limit (HEL)) indicating a better sensing ability for low hydrogen concentrations based on the LSPR shift. This LSPR redshift is inconsistent with existing models describing the LSPR frequency according to Eq. (1):

$$\omega_{LSPR} = \sqrt{\frac{ne^2}{(\varepsilon_0 m_e(\varepsilon_\infty + k\varepsilon_m))}} \qquad (1)$$

where ω_{LSPR} is the angular frequency at resonance condition, n is free carrier concentration, e is the electronic charge, ε_0 is vacuum dielectric constant, ε_m is medium dielectric constant, ε_∞ is the high-frequency dielectric constant and m_e is the effective mass of the electron [9]. In the Pd/MoO_3 films, after dissociation of hydrogen to protons over the Pd catalyst layer, they diffuse into the lattice and create defects thereby enhance the carries concentration, leading to appearing LSPR band at lower wavelength. As can be seen, the appeared LSPR blue shifts as the gas concentrations increase from 0.2-4% and then saturates at higher values.

4. Summery

Flame synthesized β-MoO_3/glass covered with Pd thin film was successfully applied for optical sensing of hydrogen gas. The sensing mechanism was based on absorption arising in the Vis to NIR LSPR due to increased carrier. The observed NIR LSPR was accompanied with the spectral shifts when hydrogen concentration changed. In overall our investigations show that the solid-fed-precursor FVD method, as an economical rout, can be applied for plasmonic doped semiconductor technology.

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