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Photoluminescence of amorphous niobium oxide films synthesized by solid-state reaction

Xiaofeng Zhou [a,b], Zhengcao Li [a], Yuquan Wang [a], Xing Sheng [a], Zhengjun Zhang [a,*]

[a] *Advanced Materials Laboratory, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China*
[b] *Department of Physics, Qujing Normal College, Qujing 655000, PR China*

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Abstract

Niobium oxide amorphous films were deposited on silicon substrates at a temperature range of 300–400 °C by heating a pure niobium foil in a rough vacuum. The films were amorphous in structure and with morphology of vertically aligned nano-columns. This feature resulted in interesting photoluminescence (PL) property in the visible light range. The intensity of the photoluminescence spectrum of the as-deposited amorphous film is small. However, the PL intensity of the same sample after annealing below 500 °C increases greatly and consists of two peaks centered at ~630 nm (1.97 eV) and ~715 nm (1.74 eV). The mechanism for the PL behavior of the amorphous niobium oxide films was also investigated and discussed.

Keywords: Photoluminescence; Amorphous niobium oxide films; Solid-state reaction

Since the niobium oxide films exhibit many excellent properties, they have been applied to various areas such as capacitors [1], wave guides [2], oxygen sensors [3], catalysts [4], etc. It is an important component in mend — alloys improving corrosion resistance [5]. Importantly, niobium oxide is used as high refractive index layers in optical interference coatings [6]. In recent years, niobium oxide has also attracted considerable interest as a promising material for electrochromic devices [7–9]. Transparent electrochromic device materials are receiving growing interest because of applications such as energy efficient windows and switchable mirrors in automobiles [10]. Niobium oxide also attracts attention due to its presence as a constituent of different compound oxides such as lead, barium and lithium niobiate, which are used in optical waveguides and modulators [11,12].

All of these technological applications of material are determined by the structures and properties of the film. Up to now, studies on the optical properties of niobium oxides were almost focused on their reflectance and refractive index properties [13–16]. In this paper, we report an interesting photoluminescence property of an amorphous NbO_x thin film and its synthesis by a thermal oxidation method.

The substrates used in this study were silicon wafers with (100) orientation. They were cleaned supersonically and sequentially in acetone, alcohol and deionized water baths, and were then fixed on a substrate holder around 2 cm above a foil of Niobium (99.9% pure, ~0.3 mm thick, ~5 mm wide and ~60 mm long) connected to two copper electrodes in a stainless steel vacuum chamber. The chamber was pumped down to 3.3 Pa and then a current of ~60 A was passed through the foil which heated up the Nb foil rapidly. The measured temperatures of the Nb foil and the substrate were 1500 °C and ~400 °C, respectively, during a deposition time of ~12 min. After deposition, the films were annealed in air for ~60 min at temperatures ranging from 100 to 600 °C.

The film morphology, structure and optical properties of the films were examined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and a photoluminescence spectrometer, respectively. The XRD apparatus was a Rigaku D/Max 2550 operated with a power of 15 kW, a scan speed of 1°/min at a step of 0.02°, using Cu Kα radiation. The measured 2θ ranged within 15–65°. XPS measurements were made using a PHI Quantera SXM photoelectron

* Corresponding author.
E-mail address: zjzhang@tsinghua.edu.cn (Z. Zhang).

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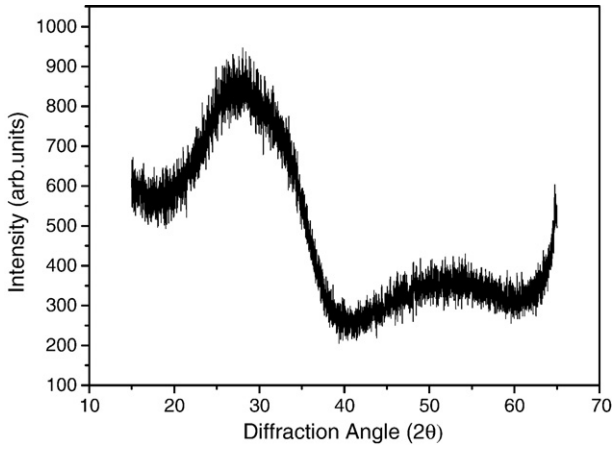

Fig. 1. XRD pattern of a typical amorphous niobium oxide.

spectrometer. The electron energy analyzer characterized by an energy resolution of 0.5 eV. An Ar ion gun was used at 4.0 kV, resulting in a 94 nm/min sputtering velocity. Four samples were introduced in the analysis chamber with a pressure of 6.7×10^{-8} Pa. The SEM was a FEI-FEG-SIRION-200 used at a voltage of 10 kV. The PL properties were measured by Renishow Raman spectrometer using a 514 nm Ar^{+} laser as the excitation source.

The deposits on silicon substrates by the above approach are amorphous niobium oxide films, which could be analyzed by X-ray diffraction (shown in Fig. 1). The amorphous structure was stable upon heating and kept unchanged after annealing at temperatures below 450 °C. Fig. 2 shows a typical SEM image of the amorphous niobium oxide grown on the silicon substrates. After deposition for ~15 min, the entire substrate was coated with a highly uniform and densely packed array of niobium oxide nano-columns, with a diameter of 20–100 nm and a length of ~300 nm, vertically aligned on the silicon substrates. Interestingly, every nano-column was composed of many small clusters.

From the PL spectra of the amorphous NbO_x films before and after annealing at various temperatures, the light emission wavelength is known to be in the range of 517–1000 nm (shown in Fig. 3). The intensity of the photoluminescence spectrum of the as-deposited amorphous film is much smaller, the maximum being approximately 8000 counts. However, the PL intensity of

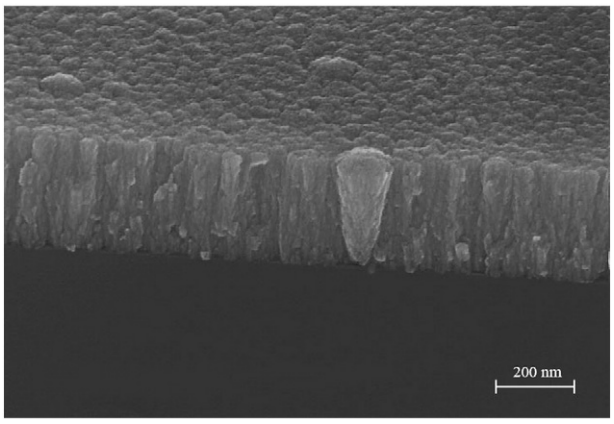

Fig. 2. SEM image of a typical amorphous niobium oxide.

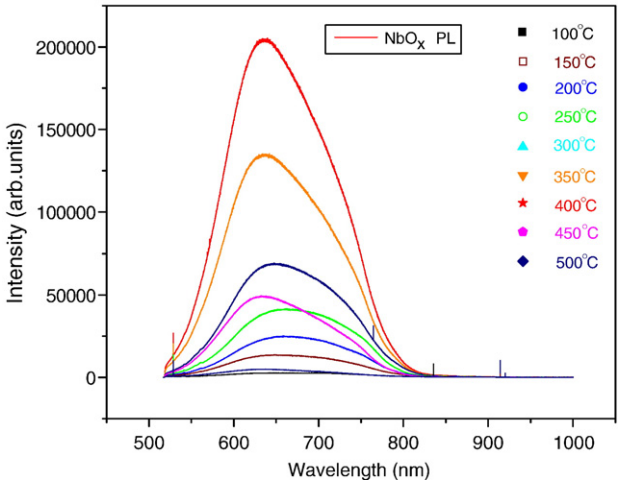

Fig. 3. PL spectra of the amorphous NbO_x films before and after annealing at various temperatures.

the same sample after annealing below 500 °C increases greatly and consists of two peaks centered at ~630 nm (1.97 eV) and ~715 nm (1.74 eV).

In order to investigate the structure and photoluminescence mechanism, further PL measurements and X-ray photoelectron spectroscopy analysis have been carried out for samples annealed at 100 °C, 200 °C, 300 °C and 400 °C, respectively. Fig. 4 shows the variation photoluminescence intensity for samples annealed temperature ranging from 150°C to 600 °C. The PL intensity increases with the annealing temperature and reached a maximum at 385 °C. After 400 °C the PL intensity dropped. Since the optical band gap of Nb_2O_5 film is ~3.7 eV [13], the emissions with a broad visible range cannot be contributed to the band gap. Through comparison of the PL spectra at different annealing temperatures, especially the analysis of XPS, the PL observed in the amorphous NbO_x films was possibly due to the formation of some defects, which could induce visible light emission.

Fig. 5(a) shows the XPS spectrum of the Nb_{3d} peak of the film annealed at 300 °C (depth of ~50 nm). The three pairs of $3d_{5/2}$ and $3d_{3/2}$ peaks are related to NbO, NbO_2 and Nb_2O_5,

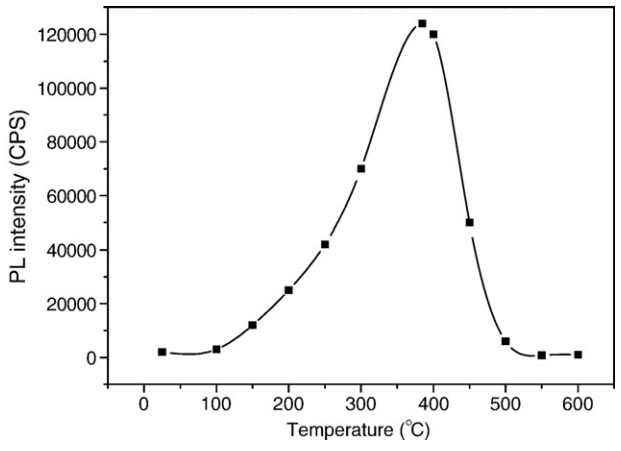

Fig. 4. Intensity of the photoluminescence peak of the amorphous films as a function of the annealing temperature.

respectively. Fig. 5(b) shows the XPS spectra of the Nb_{3d} peak of the films annealed at different temperatures (100, 200, 300 and 400 °C). The relative contents of NbO, NbO_2 and Nb_2O_5 calculated by fitting the peaks are shown in Fig. 6. The niobium oxides of low valence are oxidized with the annealing temperature, so that the content of Nb_2O_5 is increased. Similar results were observed from previous research [13], where Venkataraj et al. showed the transformation from amorphous NbO_x suboxides to Nb_2O_5. The transitions were described with the equations below:

$$2NbO + \frac{3}{2}O_2 \rightarrow Nb_2O_5$$

$$2NbO_2 + \frac{1}{2}O_2 \rightarrow Nb_2O_5$$

This suggests that upon heating in the air, NbO_x suboxides could be further oxidized into Nb_2O_5, and that the PL was not originated from NbO_x suboxides, as the as-deposited film contained more NbO_x suboxides and its PL intensity is the weakest. The phase transformation from NbO_x suboxides into Nb_2O_5, in the authors' opinion, should be responsible for the observed enhanced visible light emission. This is also in agreement with the curve of the maximum intensity of the photoluminescence peak of the amorphous films as a function of the annealing temperature of the NbO_x films shown in Fig. 4. At low annealing temperatures, e.g., <400 °C, many defects are available in the newly formed Nb_2O_5 and their amount increases with the annealing temperature, thus leading to an enhanced PL. When the annealing temperature is near the phase transition temperature (~400 °C), a maximum amount of defects are induced through the intense structural changes (such as atomic diffusion and dislocation slippage). However, at high annealing temperatures, e.g. >450 °C, the amount of defects decreased, thus the PL intensity was weakened.

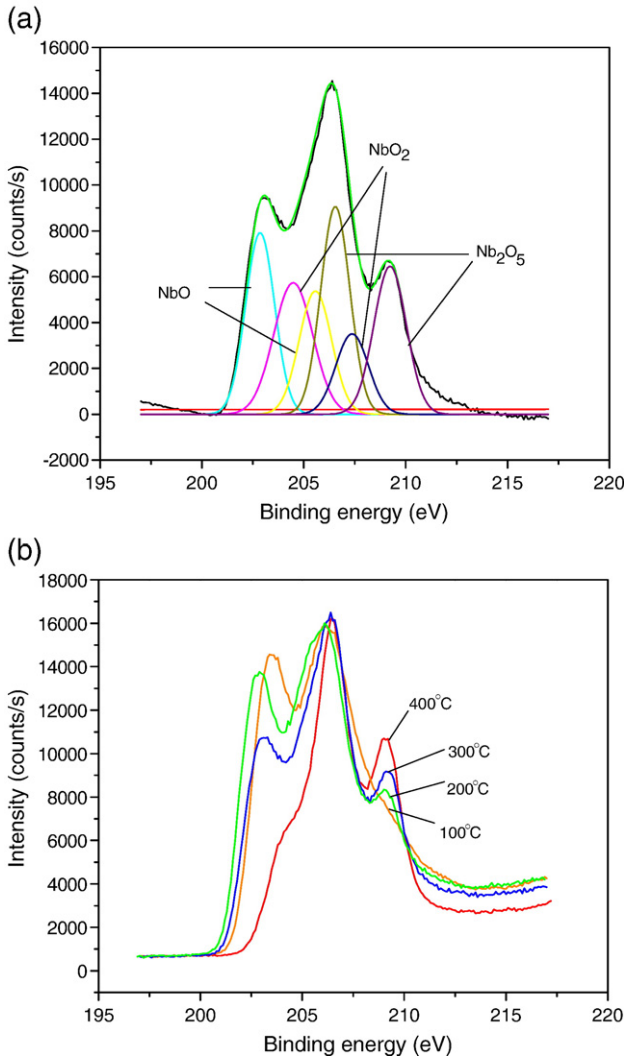

Fig. 5. XPS spectra of the Nb3d peaks of the films annealed (a) at 300 °C and (b) at different annealing temperatures at a depth of ~50 nm.

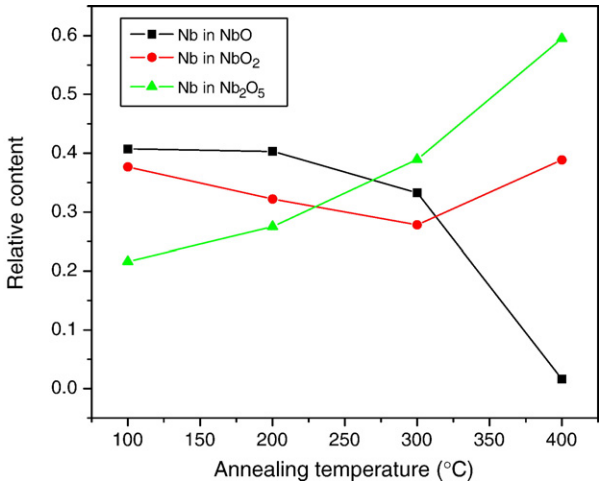

Fig. 6. Curve of atomic ratio of Nb bonded to NbO, NbO_2 and Nb_2O_5 in samples annealed at different temperatures at a depth of 50 nm.

In summary, a simple method to prepare amorphous niobium oxide films that emit visible light at room temperature has been developed. The intense PL was probably due to the defects in the films, and the intensities of the PL spectra changing with the annealing temperature were related to the amount of the defects induced by the phase transition.

Acknowledgments

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