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Growth and characterization of ultrathin TiO_2-Cr_2O_3 nanocomposite films

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Abstract: This paper presents growth of TiO_2-Cr_2O_3 nanocomposite ultrathin films (~30 nm thick) by sputtering technique for gas sensor applications. The deposited films were annealed to grow rutile TiO_2 and eskolaite Cr_2O_3 phases. Grain sizes of the pristine Cr_2O_3 and TiO_2 films (45-50 nm) were found to be larger compared to the nano-composite (7.1–69.5% Cr_2O_3 in TiO_2) films (15-40 nm). The Raman spectra of the pristine TiO_2 film showed peaks at 220 cm^{-1}(B_1g), 435 cm^{-1} (Eg) and 610 cm^{-1} (A_1g) are attributed to the rutile phase of TiO_2. The pristine eskolaite Cr_2O_3 layer exhibited four Eg peaks at 300 cm^{-1}, 350 cm^{-1}, 520 cm^{-1} and 620 cm^{-1} along with the characteristic intense peak at 551 cm^{-1} (A_1g mode). The peak positions of the A_1g mode (Cr_2O_3) and Eg mode (TiO_2) are found to be red shifted from its characteristic peak positions; but no shift is detected due to the intermixing of Cr_2O_3 and TiO_2 phases. However, the FWHM of the A_1g mode is found to be increased from 9 cm^{-1} (pristine Cr_2O_3) to 13 cm^{-1} (26.1 % Cr_2O_3); while the Eg mode is found to be increased from 48 cm^{-1} (pristine TiO_2) to 80 cm^{-1} (46.9 % Cr_2O_3) due nanocomposite formation between the rutile and eskolaite phases.

Keywords: oxide materials; vapor deposition; thin films; X-ray diffraction; optical spectroscopy;

1. Introduction

In last few decades, nanostructured metal-oxides, characterized by small grain size (100 nm or less) and large surface area have received significant attention in numerous applications [1-8]. Thin films of metal-oxides such as ZrO_2, TiO_2, HfO_2, MgO, ZnO, Cr_2O_3, $Pb(ZrTi)O_3$, and $BiFeO_3$ etc. are extensively used in metal-oxide-semiconductor field effect transistor (MOSFET), optical filters, thin film capacitor, protective and thermal barriers, chemical sensors, microelectromechanical system, superconductor, multiferroic and other diverse areas [2, 4, 8, 9-15].

Among these applications, there is a huge demand for good quality ultrathin (<50 nm) metal oxide films (like ZrO_2, TiO_2, HfO_2 etc.) in current MOSFET technology to replace SiO_2 as gate insulators [1-2, 4, 6, 8-9, 16]. Titanium dioxide (TiO_2) is one of the most promising materials in the field of MOSFET technologies due to its superior dielectric properties and excellent thermal, chemical and mechanical stability with semiconductors (Si and GaAs) [2, 4, 8-9, 16-17]. TiO_2 has three types of crystallographic phases - anatase, brookite, and rutile. Among them, rutile phase possesses a higher value of dielectric constant (ε~80) compared to the other two phases and also thermodynamically more stable [6-10, 17-19]. The TiO_2 thin films are also being used as photo-catalytic materials [2-3, 17-19].

On the other hand, nanostructured chromium (III) oxide (Cr_2O_3) with high specific surface area has drawn considerable attentions in wide variety of sensing applications [20-29]. Among the different chromium oxide solid phases, chromia (Cr_2O_3) is the only solid chromium oxide phase stable at temperatures above 500 °C;