Nanostructure control of 2D van der Waals Materials α-MoO_3

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Molybdenum oxides (MoO_x) are one of interesting oxides in various applications such as chemical catalysis, bio-sensing, and photovoltaic devices [1]. In particular, α-type MoO_3 (α-MoO_3) is known as a two-dimensional (2D) van der Waals material, which provides low-dimensional electrical and optical characteristics. Additionally, control of the reduction of Mo elements causes change in electronic states from transparent insulating to semi-metals, which produces highly tunable and versatile applications. So far, growth related to α-MoO_3 films and nanostructures are reported some papers [2]. However, studies of the controlled synthesis of α-MoO_3 films and nanostructures are still limited. In this presentation, we report on growth of α-MoO_3 nanostructured films and their related materials.

	Mo oxidation states (%)			
Pressure (O_2)	Mo^{+VI}	Mo^{+V}	Mo^{+IV}	Average formula
15 Pa	100%	—	—	MoO_3
12.5 Pa	90.1%	9.9%	—	$MoO_{2.95}$
10 Pa	89%	11%	—	$MoO_{2.94}$
7.5 Pa	82.1%	17.9%	—	$MoO_{2.91}$
5 Pa	74.3%	25.7%	—	$MoO_{2.87}$
2.5 Pa	27%	59.1%	13.9%	$MoO_{2.56}$
1 Pa	19.2%	38.8%	41%	$MoO_{2.37}$
0.1 Pa	10.8%	42.3%	46.9%	$MoO_{2.32}$

Table 1. XPS results for MoO_x nanostructured films on the stepped STO substrates.

α-MoO_3 nanostructured films were grown on TiO_2-terminated $SrTiO_3$ (100) substrates due to small lattice mismatch between α-MoO_3 (010) and $SrTiO_3$ (100) by pulsed laser deposition (PLD). The x-ray diffraction (XRD) revealed that the film sample grown under high O_2 pressure of 10 Pa showed a single crystal of α-MoO_3 along the [010] direction from the result of 2D reciprocal space mapping, which was also confirmed by μ-Raman scattering. Firstly, the effect of O_2 pressure on the chemical composition of MoO_x was investigated using x-ray photo-emission spectroscopy (XPS). The reduction of O_2 pressure from 15 Pa to 0.1 Pa provided remarkable change in valence states of Mo elements (Mo^{6+}, Mo^{5+} and Mo^{4+}) [Table 1]. Chemical ratios of the Mo^{5+} and Mo^{4+} states gradually increased with reducing O_2 pressure as a result of the decrease in the Mo^{6+} state. Besides, we observed morphologies on the film surfaces using scanning electron microscopy (SEM). The high O_2 pressures at 10 Pa clearly showed nano-needle structures. However, the decrease in O_2 pressure caused change in morphology from nano-needle structures to elongated nanowire structures. The sample grown under a low O_2 pressure of 0.1 Pa showed a smooth surface with a roughness of 5 nm. We succeeded to fabricate nanostructured films of α-MoO_3 under the high O_2 pressures by PLD. Hereafter, we will progress plasmonic biosensing applications based on MoO_x/MoO_3 nanostructures. MoO_x with low valence states of Mo elements has metallic properties in the visible range, which are expected for surface-enhanced Raman scattering (SERS).

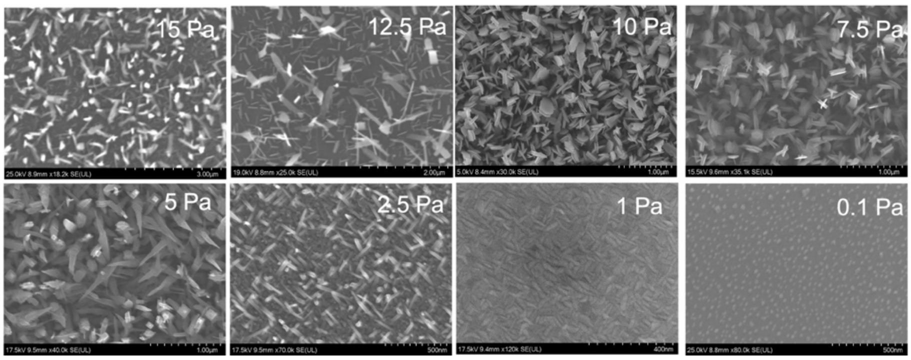

Figure 1. SEM results for MoO_x nanostructured films on the stepped STO substrates.

Reference:

[1] de Castro I A, Datta R S, Ou J Z, et al. Molybdenum oxides–from fundamentals to functionality[J]. Advanced Materials, 2017, 29(40): 1701619.

[2] Gao Q, Wang S, Fang H, et al. One-dimensional growth of MoOx-based organic–inorganic hybrid nanowires with tunable photochromic properties[J]. Journal of Materials Chemistry, 2012, 22(11): 4709-4715.