Atomic layer deposited cobalt oxide thin films as photoanodes for photoelectrochemical water splitting

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Cobalt oxides have attracted a great interest in view of their potential applications including electrochromic devices, sensors, ReRAM, catalysts and intercalation compounds for energy storage due to their useful electronic and magnetic properties. Cobalt oxide is known to exist in two different stable phase, one is Co_3O_4 that is mixed valence compound $Co^{II}Co^{III}{}_2O_4$ with the normal spinel structure. The other thermodynamically stable oxide is the high temperature phase CoO which crystallizes in a rocksalt structure at temperature above 900°C, however kinetically stable at room temperature. Co_3O_4 is more beneficial as an intercalation host material because spinel structure has a larger unit cell (0.808 nm) than the rock-salt structure (0.427 nm) and contains more interstitial sites. Co_3O_4 is the corresponding electrochromic efficiency is relatively high (≈25 cm^2,C^{-1}). And also, it can offer large surface area, high conductivity, electrochemically stability. Various kinds of thin film deposition techniques, including such as sputtering, CVD, PLD and ALD have been used for obtaining single-phase Co_3O_4 thin film. But the most of previous studies showed that thin films with dual-phased of CoO and Co_3O_4 were deposited. In the case of ALD, a single-phased Co_3O_4 thin film was obtained only when the very reactive oxidant O_3 or O_2 plasma were used and in case of O_2 molecules, very high temperature was required. It means that it have been difficult to obtain single phase Co_3O_4. In this study, at first, the controlled growth of various cobalt oxides thin films was investigated by ALD using a novel Co metallorganic precursor and O_2 molecules as a reactant at a deposition temperatures ranging from 125 to 300 °C. XRD and Raman analysis indicated that deposition temperature range from 125 and 250 °C, CoO and Co_3O_4 dual-phased thin film was deposited. And, a single-phased Co_3O_4 was formed from temperature at 265 °C. The RBS analysis indicated that at 275°C, almost stoichiometric Co_3O_4 thin film was deposited. From UV-Visible analysis, a single-phased Co_3O_4 film optical band gap was determined as 1.98 eV. The ALD cobalt oxides thin films prepared in this study were evaluated as a heterojunction p-CoO_x/n-Si photoanode for photoelectrochemical (PEC) water splitting.

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