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Frequency-dependent conductivity in tris(acetylacetonato) manganese(III) thin films on Si(1 0 0) substrates

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Abstract

Thin tris(acetylacetonate)manganese(III) films of amorphous structure were prepared by vacuum deposition on glass and Si (1 0 0) substrates. The as-deposited and annealed-in-vacuum films were characterised by X-ray fluorescence, X-ray diffraction and optical absorption spectroscopy. The prepared title-complex amorphous films were investigated as insulators for Al/insulator/Si(P) metal–insulator–semiconductor (MIS) structures, which were characterised by the measurement of their capacitance and AC-conductance as a function of gate voltage. From those measurements, the state density D_{it} at insulator/semiconductor interface and the density of the fixed charges in the complex insulator were determined. It was found that D_{it} was in order of 10^{11} eV^{-1} cm^{-2} and the surface charge density in the insulator film was in order of 10^{11}–10^{12} cm^{-2}.The frequency dependence of the electrical conductivity and dielectric properties of MIS structures were studied at room temperature. The results follow the correlated barrier-hopping (CBH) model, from which the fundamental absorption bandgap, the minimum hopping distance and other parameters of the model were determined. This study shows that the tris(acetylacetonate)manganese(III) films grown on Si(1 0 0) is a promising candidate for high-ε dielectric applications. It displays sufficiently high-ε value in the range 30–40.

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Keywords: Insulating films; Tris(acetylacetonate)manganese(III); Dielectric phenomena; CBH model

1. Introduction

The metal ions in metal-substituted organic coordination complexes (MOSC) play a role of attraction centres through strong metal–ligand covalent bonds [1], which enhance the stability of the molecules even under sublimation. Among these MOSC is the dark-brown tris(acetylacetonato)manganese(III) or tris(2,4-pentanedionato)manganese(III), which has several CHEMICAL applications like polymerisation of vinyl monomers, combustion catalyst, curing agent for isocyanate resins and deposition of manganese oxide. Its molecular structure can be described as follows: one acetylacetonate anion [abb. acac: $(CH_3COCHCOCH_3)^-$] serve as a ligand to a metal ion, forming chemical structure in which the ligand is bonded to the metal ion through both oxygen atoms forming a planer six-membered ring (Mn-O_2C_3) [2]. This binding can be thought of as consisting of a covalent bond through one oxygen atom and a dative-covalent bond through the other oxygen and this bonding is delocalised. In the complex of molecular stoichiometry $Mn(acac)_3$, each Mn ion is bonded to three acac radicals, so that the Mn-O_6 array forms an octahedral coordination polyhedron, which suffers from Jahn–Teller distortion in form of either a tetragonal elongation (TE) (two Mn–O = 0.212 nm; four Mn–O = 0.193 nm) or a moderate tetragonal compression (TC) (two Mn–O = 0.195 nm; four Mn–O = 0.200 nm) [1–3]. In the solid state, the complex molecules arrange themselves in three different crystal structures (α, β and γ [2,4]) depending on the preparation conditions. The starting material in the present investigation is the familiar β-phase of a monoclinic structure ($P2_1/c$) with $a = 1.4013$ nm, $b = 0.76$ nm, $c = 1.6373$ nm and $\beta = 99.33^\circ$ [2].

In the present investigation, we have prepared the title-complex thick films by sublimation in vacuum on Si(1 0 0) substrates and report here on their AC-electrical properties as

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a function of frequency. This well-known coordination complex has not been studied before by AC-electrical method.

2. Experimental details

The synthesis of crystalline tris(acetylacetonato)manganese(III) powder has been described in detail elsewhere [5]. Thin films of the complex (Mn-acac) were slowly deposited (about 0.1 nm s^{-1}) by thermal sublimation using Mo boat in a vacuum system of about 10^{-3} Pa on Si(1 0 0) substrates held at room temperature. The boron-doped at level of 1.2×10^{22} m^{-3} Si wafer substrates were thermo-chemically cleaned with 50% potassium hydroxide solution at 65 °C for 15 min. Two sorts of Mn-acac layers were investigated; namely the as-deposited and the annealed in vacuum of about 10^{-3} Pa at about 100 °C for 10 min. The annealing was done in order to produce microstructural variations to reduce the density of the trapped charges in the deposited layers. The electrical measurements on the title-complex layers as insulators were done on samples prepared in form of metal–insulator–semiconductor MIS structures, which constructed by deposition of aluminum-film electrodes of about 150 nm. The complex layer thickness was measured by Gaertner L117 ellipsometer of $\lambda = 632.8$ nm to be about 495 nm with refractive index of about 1.3.

The Mn content in the deposited film samples and the constituent powder was probed by the X-ray fluorescence (XRF) method. The exciting Ni-filtered X-ray Cu radiation ($\lambda = 0.15405$ nm) was incident on the film surface at 15° and the fluorescent yield was collected at 90° by using an Amptek XR-100CR, Si detector. The crystal structure was investigated with a Philips PW 1729 X-ray diffractometer using Cu Kα radiation with a scanning speed of 0.01° s^{-1}. The AC-electrical measurements were performed using a Keithley 3330 LCZ instrument with a signal of 50 mV and the DC-measurements were carried out with a Keithley 614 electrometer.

3. Characterisation details

3.1. Mn-acac films characterisation

Fig. 1 shows the XRF spectrum of Mn-acac powder and thin film grown on Si substrate. There are two considerable peaks; namely a Si Kα signal of energy 1.74 KeV and a Mn Kα signal of energy 5.898 keV. The appearance of the Mn signal radiated from the deposited thin film ensures the stability of Mn-acac molecules during the sublimation at about 150 °C.

Fig. 2 shows the X-ray diffraction (XRD) pattern of the prepared $Mn(acac)_3$ powder, which shows a monoclinic structure of parameters $a = 1.41$ nm, $b = 0.77$ nm, $c = 1.65$ nm and $\beta = 99.4°$ that are almost comparable to those given in Ref. [2] for the β-phase. The XRD patterns of both the as-deposited and the annealed thin films show amorphous structure.

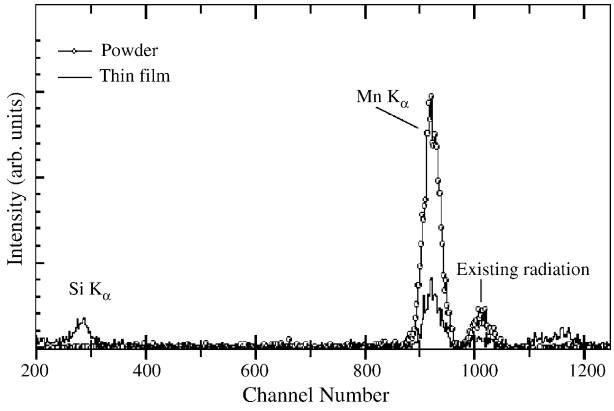

Fig. 1. XRF spectrum of tris(acetylacetonate)manganese(III) powder and thin film grown on Si substrate. The exciting line was Cu Kα line of energy 8.047 keV.

The spectral normal transmittance $T(\lambda)$ of the amorphous Mn-acac film grown on glass substrate in the transparent and absorption regions (200–1100 nm) was measured by UV–VIS-Shimadzu double beam spectrophotometer and the results are shown in Fig. 3. The transmittance data were corrected relative to the optically identical uncoated substrate. The investigated sample has high transparency $T > 0.90$ in the transparent region and a sharp absorption edge, which refer to the direct transitions. The energy gap was calculated according to the method discussed in Ref. [6] and using Hamberg et al. absorption relation [7], to be about 3.66 eV.

3.2. Capacitance–voltage analysis

Prior to AC-electrical conductivity measurements, the constructed MIS structures should be electrically characterised by measuring their high-frequency capacitance as a function of gate voltage. Those measurements determine the effective relative permittivity (RP) of the insulating layer, the

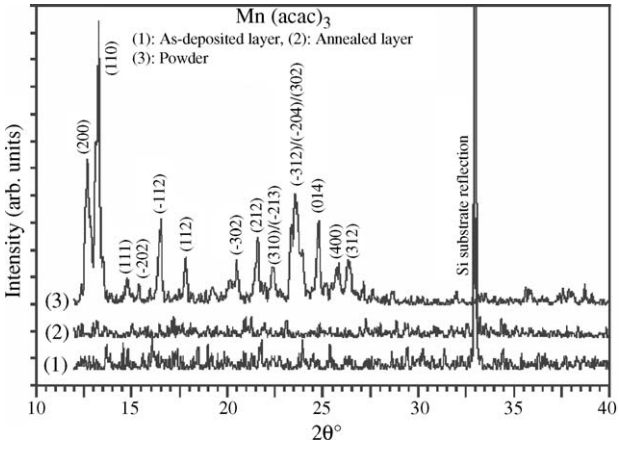

Fig. 2. X-ray diffraction of tris(acetylacetonate)manganese(III) powder and thin film. The beam was Cu Kα and the scan speed was 0.01° s^{-1}.