Epitaxial $KNbO_3$ films grown by pulsed injection MOCVD

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RÉSUMÉ

The issues of the limited volatility of K precursors, available in the industry, in the synthesis of $KNbO_3$ films by means of metal-organic chemical vapor deposition, have been addressed by using the advanced $K_4(hfa)_4$tetraglyme precursor. The epitaxial growth of $KNbO_3$ films with controlled K stoichiometry has been demonstrated on different substrates.

MOTS-CLEFS : *$KNbO_3$; thin films ; CVD.*

1. INTRODUCTION

Among the large family of ferroelectrics, the perovskite-type $KNbO_3$ has attracted a considerable interest in the field of agile dielectric devices and for its electro-optic and acoustic properties. However, the synthesis of $KNbO_3$ single crystals is very challenging and only very expensive single crystals with small size are available at present. To bring this material towards industrial applications, the only remaining possibility is to use the grown $KNbO_3$ thin films. Nevertheless, the growth of $KNbO_3$ is far from being a routine process due to high volatility and reactivity of K_2O. The chemical deposition methods, enabling better control of volatile element composition, face a difficulty in finding a reliable K precursor. The industrially available K precursors present low volatility or high instability at ambient conditions.

In this paper, we report the use of an advanced K precursor, the $K_4(hfa)_4$tetraglyme adduct, enabling a better control of K stoichiometry in $KNbO_3$ films. The epitaxy of the $KNbO_3$ films was studied on C-sapphire, R-sapphire, and 36°Y-$LiNbO_3$ (36°Y-LN) substrates by means of X-ray diffraction.

2. EXPERIMENTAL DETAILS

KN films on C-sapphire, R-sapphire and 36°Y-$LiNbO_3$ substrates (supplied by Roditi) were deposited by pulsed-injection metalorganic chemical vapor deposition (MOCVD)—a method providing digital control of the film deposition. Mixtures of $K_4(hfa)_4$tetraglyme-$Nb(thd)_4$, dissolved in 1,2-dimethoxyethane, were used for the growth of $KNbO_3$ films, where thd = 2,2,6,6-tetramethyl-3,5- heptanedionate and hfa = hexafluoroacetylacetonate. Micro-doses of solution were injected into a hot evaporator with a frequency of 0.5 Hz, and vapour was transported to a hot substrate by a mixture of Ar and O_2 (33%) gases. The deposition temperature was 700 °C. The phase composition and the texture have been analysed by means of X-ray diffraction (XRD). The symmetry of the films has been defined by using polarized Raman spectra measurements. The surface morphology and the elemental composition were studied by means of surface scanning microscopy (SEM) and energy dispersive X-ray analysis (EDX). The stereographic projections have been visualized by using Winwulf software.

3. RESULTS

The $KNbO_3$ films, grown by using the advanced K_4(hfa)$_4$tetraglyme and the standard Nb(thd)$_4$ precursors, presented a K/Nb ratio close to 1, as indicated by EDX analysis. The film texture and morphology was highly depending on the substrate (Fig. 1). In the case of R-sapphire substrates, a mixture of 110 & 001 with presence of 111 orientation have been obtained. The morphology of these films consisted mainly of squares rotated by 90° and 45° in the substrate plane with respect to each other. In the case of C-sapphire, the dominating orientation was 201, which presents triangular growth symmetry, which can be identified in its stereographic projection (Fig. 1i), as well. The purest growth texture was obtained on 36°Y-LN substrates, which is clearly identified from the homogeneously oriented squares in the morphology (Fig. 1e) and XRD pattern (Fig. 1b).

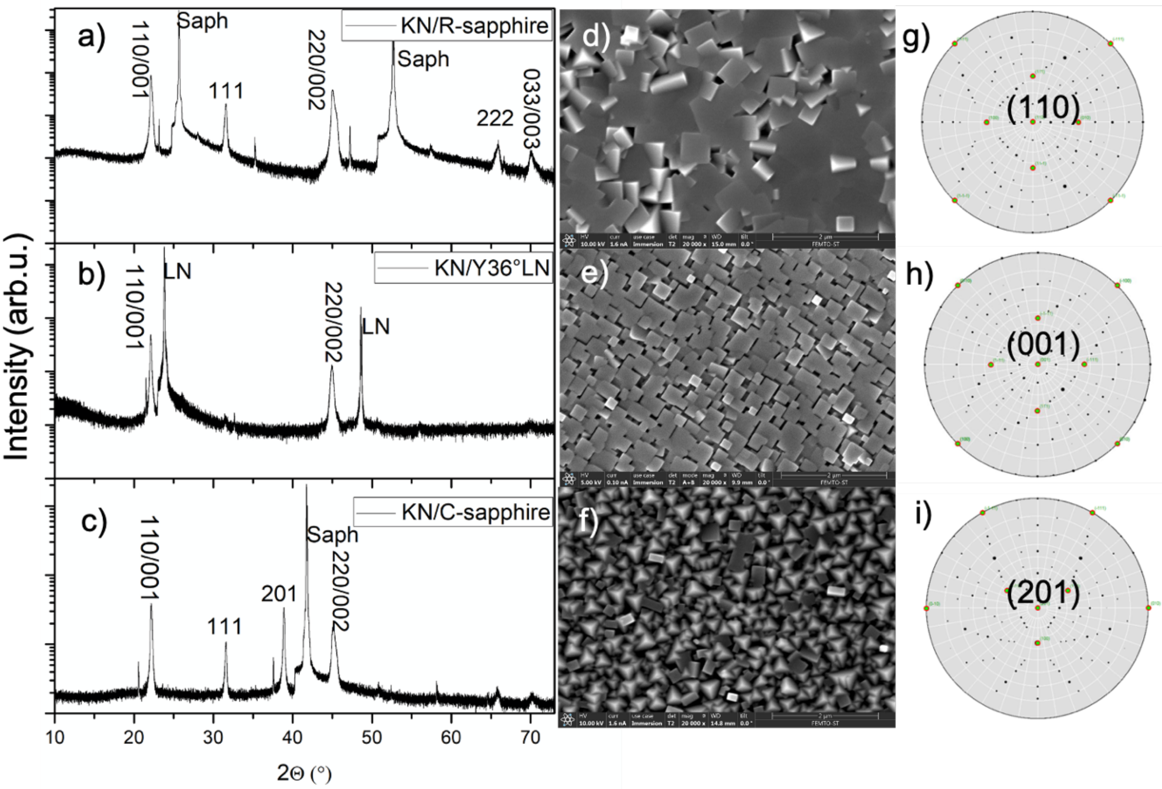

Fig. 1 : XRD patterns (a, b, c) and SEM images of morphology (d, e, f) of $KNbO_3$ films grown on R-sapphire, 36°Y-LN, and C-sapphire substrates, respectively. Stereographic projections of (110), (001), and (201) planes of orthorhombic $KNbO_3$ (g, h, and I, respectively).

CONCLUSION

A better control of K:Nb stoichiometry in $KNbO_3$ films has been demonstrated by using the K_4(hfa)$_4$tetraglyme precursor with respect to the industrially available K(thd) precursor. This enabled to attain nearly stoichiometric $KNbO_3$ films and their epitaxial growth on different substrates.

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