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Deposition of highly oriented (K,Na)NbO_3 films on flexible metal substrates

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Abstract

In view of developing flexible, highly textured Pb-free piezoelectric thin films, (K,Na)NbO_3 was deposited by chemical solution deposition on cube-textured Ni-W alloy substrates. After heat treatment, a strong $(001)_{pc}$ out-of-plane preferential orientation is created in the (K,Na)NbO_3 layer, which also exhibits a sharp in-plane texture with 45°-rotated epitaxial relation to the substrate . The microstructure of the film is strongly dependent on the heat treatment temperature; sub-micrometer grains versus up to 2 μm long particles forming at 600°C and 900°C respectively. $K_4Nb_6O_{17}$ and $(K_{1-x}Na_x)_2Nb_4O_{11}$ impurity phases were identified depending on the processing temperature.

Keywords: Piezoelectric materials; Thin films; Sol-gel preparation; Texture

1. Introduction

Owing to its high Curie temperature, biocompatibility, high dielectric and piezoelectric properties, $(K,Na)NbO_3$ (KNN) is a promising materials for replacing lead-based piezoelectric compounds. As shown by Saito et al. [1], preferential orientation of the KNN crystallites is a key microstructural parameter for performance optimization. Highly $(001)_{pc}$ (pc = pseudo cubic) oriented KNN films have already been demonstrated on substrates such as Pt/MgO [2], $Pt/Ti/SiO_2/Si$ [2] and $SrRuO_3/SrTiO_3$ [3]. However, these substrates cannot be bent, while applications of piezoelectric films in e.g. energy harvesters, would benefit from the use of a flexible substrate. Flexibility can be achieved by using organic substrates [4] but this kind of substrate does not induce significant preferential orientation in the piezoelectric layer. Shiraishi et al. [5] demonstrated $(001)_{pc}$ textured KNN films on 300 μm thick inconel flexible foils with conductive $SrRuO_3/LaNiO_3$ buffer layers. It would therefore be interesting to deposit the piezoelectric film directly on top of a metal substrate that could play the role of bottom electrode to simplify the architecture of the assembly. Recently, Milhim and Ben-Mrad [6] successfully grew KNN films on a Ni electrode by sputtering. These films show promising characteristics and demonstrate the chemical compatibility of KNN and Ni, but are not $(001)_{pc}$ oriented. Developments in the processing of high-temperature superconducting tapes have shown that cube-textured Ni-based alloys can be used as templates for growing preferentially oriented ceramic thin films [7]. The present work was undertaken as a proof-of-concept study to demonstrate that this approach can also be applied to the manufacture of textured KNN films directly on flexible, electrically conductive substrates.

2. Experimental

The cube textured metal substrates were purchased from Evico GmbH. They consist of fully recrystallized Ni – 5% W alloy tapes (Ni5W) with 70 μm thickness, 1 cm width, grain size 20-50 μm. The substrates used in the present work were cut from a 10 m long tape to form 1x1 cm^2 square-shaped pieces. The coating solution was prepared by dissolving Nb-ethoxide into propionic acid, followed by the addition of dried Na_2CO_3 and K_2CO_3 in stoichiometric amounts corresponding to a $K_{0.5}Na_{0.5}NbO_3$ composition with a cation concentration of 0.28 M. Spin coating was performed with 5000 rpm during 1 min. After drying at 100°C for 15 min, the films were heated in flowing 5 % H_2 – 95 % Ar for 10 min at temperatures ranging from 500°C to 900°C (heating rate = 180°C/h) and furnace cooled. For comparison with films made by a single coated layer, a film was coated 3 times with heat treatment at 900°C after each coating operation.

X-ray diffraction (XRD) patterns were collected in a Bruker D8 diffractometer using Cu Kα radiation in θ-2θ geometry. Scanning electron microscope (SEM) studies and electron backscatter diffraction (EBSD) measurements were performed on a Zeiss Merlin field emission gun SEM (FEGSEM) equipped with an Oxford Instruments Nordlys II S EBSD detector. Cross-sectioning and imaging was performed in a Zeiss 1540 CrossBeam focused ion beam – SEM. equipped with an X-ray energy dispersive spectrometer (EDS operated at 15 kV with 5mm distance and 35° take off angle) and microanalysis software NSS (Thermo Fischer Scientific) used for elemental analysis. EBSD data collection and analysis was performed with CHANNEL 5. The film being very thin, EBSD was performed at an accelerating voltage of 8 kV to minimize the Ni alloy substrate's contribution to the electron beam interaction volume and therefore minimize the degree of Kikuchi pattern overlap of different phases.

The mechanical properties of nickel-based textured metals substrates are usually evaluated in terms of resistance to axial stress. For energy harvesting applications involving vibrations in a direction perpendicular to the plane of the substrate, information about the critical bending radius at the limit between elastic and plastic deformation would be more relevant. Such data being not available, we evaluated the elastic limit of the substrates by bending 10 cm long tapes around cylinders with progressively smaller diameter. The critical bending radius was determined as the mean value of the radius of the smallest cylinder allowing the tape to recover its original shape and that of the largest, which resulted a non-elastic behaviour (i.e. the tape could not recover its original shape after release of the deformation). The results of several measurements showed that the critical bending radius was equal to 2.2±0.2 cm for the tapes used in the present investigations.

3. Results and discussion

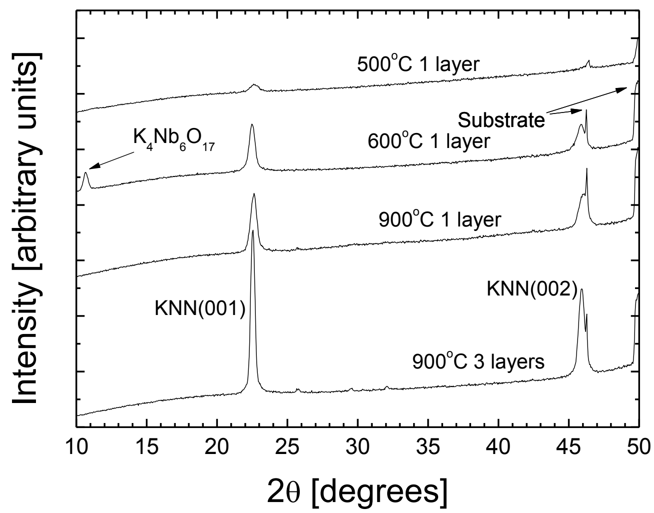

Figure 1: XRD patterns of films processed at different temperatures.

Figure 1 shows the XRD patterns of samples heat treated at different temperatures. Low intensity diffraction peaks that can be identified as the $(001)_{pc}$ and $(002)_{pc}$ reflections of KNN are already apparent for the film annealed at 500°C. Increasing the sintering temperature to 600°C results in more intense and narrower peaks. Only $(00l)_{pc}$ peaks are seen for the KNN phase, indicating a very strong preferential orientation. However, an extra diffraction peak is visible at $2\theta = 10.8°$ after processing at 600°C. It could be due to the presence of $K_4Nb_6O_{17}$ impurities. This is the only visible peak that can be attributed neither to KNN nor to the substrate so we may conclude that $K_4Nb_6O_{17}$ also has a strong preferential orientation. This is not surprising since $K_4Nb_6O_{17}$ has a layer structure and forms plate-shaped crystallites. The presence of this impurity phase has previously been reported in KNN thin films prepared by chemical solution deposition methods [8] and it is known to appear as an intermediate phase during the reaction leading to the formation of KNN at 600°C [9]. Nevertheless, the impurity XRD peak disappears upon increasing the processing temperature to 900°C.

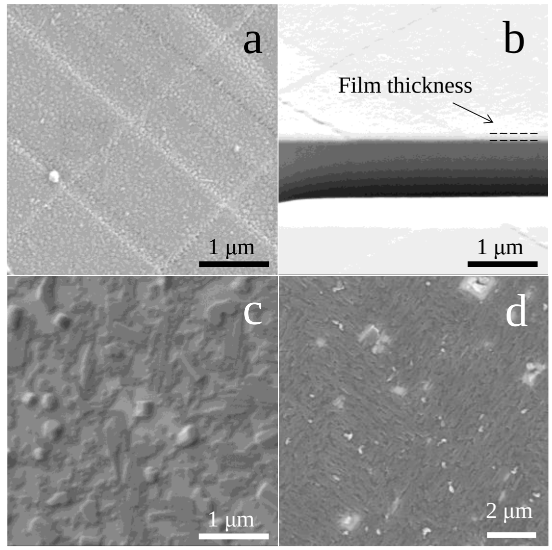

Figure 2: SEM images of the films after heat treatment. (a) 600°C, (b) 600°C cross-section, (c) 900°C 1 layer, (d) 900°C 3 layers.

A SEM image of the surface of the film sintered at 600°C is shown in Fig. 2a. The straight lines crossing at right angles and oriented 45° relatively to the rolling direction of the metal substrate are annealed remnants of the deformation structure that cause surface roughening upon annealing during production of the Ni5W substrate tape. The film consists of fine grains of about 50 nm diameter similar to the film thickness (~120 nm), estimated from the cross-section view in Fig. 2b. As evidenced in Fig. 2c, sintering at 900°C induces KNN grain growth and coalescence, which result in uncovered substrate areas (light gray places between the darker KNN particles). The latter drawback can be avoided by depositing several KNN layers as shown in Fig. 2d for a film with 3 consecutive layers sintered at 900°C. In this film, most particles are elongated and appear to form areas, where grains are aligned in the plane but with an angle of 90° between these areas. These elongated particles can be identified as KNN with a clear K deficiency: K/Na atomic ratio = 0.45 ± 0.27 instead of 1 in the nominal composition. Besides, there are a few lighter particles found by EDS to have a (K+Na)/Nb atomic ratio = 0.52 ± 0.06, which corresponds $(K_{1-x}Na_x)_2Nb_4O_{11}$, here with x close to 0.5. The alkaline-deficient secondary phases and the reducing atmosphere used for the heat treatment are expected to induce leakage current [10]. Improvements can be expected from the use of K and/or Na excess in the starting solution [10], reduction of the sintering temperature by e.g. deposition of a V_2O_5 seed layer [11], doping with elements such as Mn [12] and/or post-annealing in oxygen like is normally done for $YBa_2Cu_3O_7$ superconducting films deposited on Ni5W substrates [13]. Reducing the sintering temperature would also be advantageous since grain growth inhibition is expected to improve the mechanical integrity of the films upon bending.

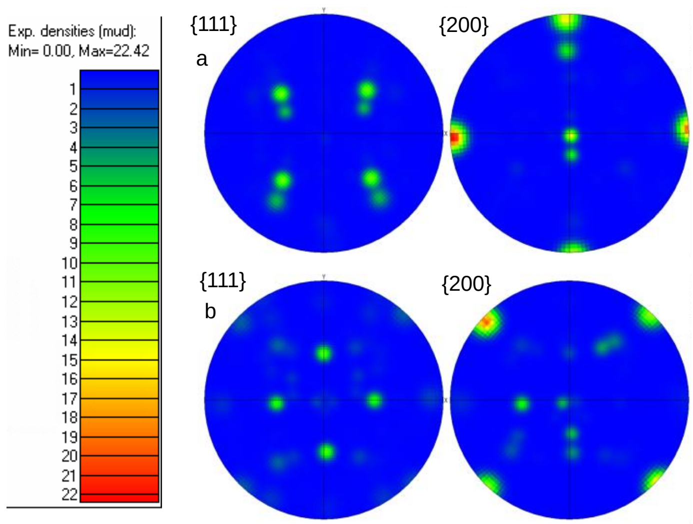

Figure 3: {111} and {200} pole figures calculated from EBSD measurements for the Ni5W substrate (upper row) and the KNN film (lower row).

Fig 3 shows pole figures calculated from EBSD orientation maps for the Ni5W substrate and the KNN film respectively for a sample with 3 layers sintered at 900°C. The thickness of the KNN film (about 150 nm) allowed the detection of Kikuchi patterns from the substrate covered with the film. The pole figures for the Ni5W substrate are typical for a cube-texture. The same characteristic distribution of high-intensity peaks can be observed for the KNN layer, but with a rotation of 45° compared with the substrate, reflecting the KNN crystal alignment observed in Fig. 2d. This feature is probably triggered by the lower lattice mismatch between the Ni5W(110) and KNN(100) planes compared to the Ni5W(100) – KNN(100) mismatch . Besides the four high intensity spots, lower intensity maxima can be seen in the pole figures corresponding to the KNN film, indicating that some crystallites with orientations differing from the (001) texture are present but in relatively much lower amount. A cube on cube epitaxial growth is not a favourable situation due to the large lattice mismatch of about 10.8 % between the respective a-axis lattice parameters of KNN (3.98 Å) and Ni5W (3.55 Å). On the other hand, there is a lower lattice mismatch (5.4 %) between the Ni5W(110) and KNN(100) planes with a reasonably close site coincidence for 2 KNN unit cells versus 3 half Ni5W cells along the diagonal of its cubic unit cell. This lattice mismatch value is however still far from ideal, which can explain the presence grains with different orientations. Using a cube-textured substrate with a larger lattice constant, e.g. a Cu-based alloy, would reduce this mismatch and may improve the in-plane texture of the KNN film. Nevertheless, the out-of-plane texture, which was achieved in the present work, is probably the most important parameter to optimise in view of piezoelectric performance.

4. Conclusion

We have demonstrated the deposition of KNN thin films with sharp out-of-plane and in-plane $(001)_{pc}$ preferential orientation directly on cube-textured metal substrates. A 45° epitaxial relation was formed between the substrate and KNN. Although further measures to avoid alkali-deficiency and leakage current might be necessary, this technique shows promise for large-scale synthesis of flexible, highly textured lead-free piezoelectrics. Further investigations are being carried out to optimize the processing parameters in order to further improve the film composition and microstructure, as well as quantifying their effect on the film's piezoelectric properties.

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Figure captions

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