J Sol-Gel Sci Technol (2013) 67:654–659
DOI 10.1007/s10971-013-3125-3

ORIGINAL PAPER

Comparison of the influence of titanium and chromium adhesion layers on the properties of sol–gel derived NKN thin films

Sebastian Wiegand · Stefan Flege · Wolfgang Ensinger

Received: 25 March 2013 / Accepted: 15 July 2013 / Published online: 27 July 2013

Abstract Lead-free $(Na_{0.5}K_{0.5})NbO_3$ (NKN) thin films were prepared on $Pt/X/SiO_2/Si$ substrates (with the adhesion promoters X = Ti, Cr) by a sol–gel process with and without post-annealing treatment. The effect of the diffusion of the adhesion layer elements Ti and Cr into the NKN film was analysed by secondary ion mass spectrometry, scanning electron microscopy pictures, X-ray diffraction (XRD), and leakage current measurements. It turned out that Cr diffuses into the films to a higher extent than Ti. The high amount of Cr diffusion led to the formation of a secondary phase, as seen in the XRD pattern, and to pore formation on the surface of the NKN films. In contrast, the films with Ti adhesion layer were single phase NKN without pore formation. Also, the leakage current measurements showed a strong influence of the Cr diffusion. The leakage current of the films with Cr adhesion layer was about four orders of magnitude higher than that of the films with Ti adhesion layer. The study shows the strong influence of the adhesion layer of the substrate on the properties of NKN films.

Keywords Sol–gel process · $(Na_{0.5}K_{0.5})NbO_3$ · Thin film · Diffusion · Substrate · Lead-free piezo material

1 Introduction

Sensors and actuators are used in many technical applications [1]. These sensors and actuators are often based on ferroelectric ceramics, with Lead-Zirconate-Titanate (PZT) possessing the biggest market share today [2]. However, PZT contains more than 60 wt % toxic lead [3] and has to be replaced because of legal regulations [4, 5] by lead-free alternatives. One candidate to replace PZT is Sodium–Potassium–Niobate (NKN) due to its high Curie temperature and favourable piezoelectric and ferroelectric properties [6].

Because of their lower driving power consumption and therefore energy saving potential there is an increasing demand for thin films [7]. There are several methods for the production of NKN thin films such as sputtering [8], pulsed laser deposition (PLD) [9], and the sol–gel process [10, 11]. Only the latter is a low cost non vacuum based method with easy scale up to mass production and the possibility of homogeneous doping [12]. The main problems for sol–gel based NKN thin films are their insufficient insulating properties and the resulting leakage current [13]. The volatility of the alkaline elements during the thermal treatment is proposed as reason for the high leakage current [14, 15]. To compensate for their loss an excess amount of the alkaline elements is given into the coating solution. But the volatility of the alkaline elements could not be the only reason for the high leakage currents of the NKN films because one can find a broad range of excess amounts, ranging from a few per cent up to 20 % excess [16], for comparable heat treatment conditions, and still the leakage currents can be high. Another important factor for thin films is the substrate. Most sol–gel based thin films are synthesized on $Pt/Ti/SiO_2/Si$-Wafers. The platinum acts as bottom electrode for the electrical characterization, the

---

S. Wiegand (✉) · S. Flege · W. Ensinger
Department of Materials- and Geo-Sciences, Materials Analysis Group, Technische Universität Darmstadt, Petersenstrasse 23, 64287 Darmstadt, Germany
e-mail: wiegand@ca.tu-darmstadt.de

S. Flege
e-mail: flege@ca.tu-darmstadt.de

W. Ensinger
e-mail: ensinger@ca.tu-darmstadt.de

titanium is an adhesion layer and the silicon dioxide acts as a diffusion barrier. Tanaka et al. [17] investigated the effect of various platinum layers on the properties of sol–gel based NKN films and found an influence on the orientation as well as on the leakage current of the films. Goh et al. [18] studied the influence of the titanium diffusion of the adhesion layer into the NKN film. It is known from PZT that the titanium diffuses into the ferroelectric film [19, 20]. For PZT films this is not a significant problem because the film already contains titanium or the zirconium ion has the same valence. In contrast, in the case of NKN films the titanium diffusion has the same effect as doping and increases the leakage current. Goh et al. [18] found that higher heating rates and higher annealing temperatures promote the titanium diffusion.

Apart from Ti, chromium is also used as transition layer to enhance adhesion. In this study we compare the influence of chromium and titanium adhesion layers on the properties of sol–gel derived NKN thin films. So far, the influence of different elements for the interlayer has not been investigated in the literature. For that purpose samples were prepared on both substrates, with and without post-annealing treatment. The degree of the diffusion was investigated by secondary ion mass spectrometry (SIMS) and the influence of the diffusion on the structure, morphology, and leakage of the NKN thin films was investigated by XRD, SEM, and leakage current measurements, respectively.

2 Experimental

For the synthesis of NKN precursor sol sodium acetate (Alfa Aesar, 99 % purity), potassium acetate (Alfa Aesar, 99 % purity) and niobiumethoxide (Alfa Aesar, 99.999 % purity) were used as metal precursors. 1,3 propanediol (Alfa Aesar, 99 % purity) and acetylacetone (Sigma Aldrich, 99 % purity) were used as solvent and as stabilizer, respectively. In the first step sodium acetate and potassium acetate were dissolved with 20 % excess amount (according to $(Na_{0.6}K_{0.6})NbO_3$) in 1,3 propanediol to compensate for their loss during thermal treatment. Next, a stoichiometric amount of niobium ethoxide was stabilized with acetylacetone. Then the two solutions were mixed and stirred for 20 h at 90 °C with a magnetic stirrer. In the last step the concentration of the solution was adjusted to 0.5 mol/L by the addition of 1,3 propanediol. The resulting sol was deposited on the two different types of substrates ($Pt/Ti/SiO_2/Si$ and $Pt/Cr/SiO_2/Si$, resp.) by spin-coating. The orientation of the silicon substrate was in both cases (100) with 200 nm thermally grown oxide. The chromium or titanium layers were sputter deposited at room temperature with a thickness of 20 nm and the platinum layer was hot sputtered at 300 °C with 150 nm thickness. A single layer of the NKN sol was deposited by spin coating at 3,000 r/min for 45 s. After the deposition the films were pyrolysed at 360 °C on a pre-heated hotplate and calcinated at 600 °C for 2 min in a pre-heated furnace in ambient air. This process was repeated four times for each NKN film. One set of samples was post-annealed for 15 min at 650 °C in a furnace. So for each substrate films with and without post-annealing treatment were synthesized, which are referred to as Cr 600 (4 times 600 °C for 2 min), Cr 600/650 (4 times 600 °C for 2 min + 650 °C for 15 min), Ti 600 (4 times 600 °C for 2 min) and Ti 600/650 (4 times 600 °C for 2 min + 650 °C for 15 min) below. The substrates were purchased from a commercial supplier (Si-Mat Silicon Materials) with 300 nm thermally grown oxide SiO_2, 20 nm Cr or Ti and 150 nm Pt.

The film thickness was measured on a partially coated sample with a profilometer (Dektak D 8000). To evaluate the diffusion of the element of the adhesion layer secondary ion mass spectrometry (SIMS, CAMECA IMS 5f) depth profiles were recorded with 8 keV O_2^+ primary ions. X-ray diffraction (XRD, Seifert 3003 PTS) measurements were used to identify the crystallographic phases of the NKN films. The measurements were performed with Cu–Kα radiation in grazing incident geometry with $\theta = 5$ deg. and a step size of 0.04 deg. with a recording time of 13 s each. The morphology of the surface was investigated by scanning electron microscopy (SEM, Philips XL 30 FEG). For the evaluation of the electrical properties of the films Au-electrodes were sputter deposited on the surface of the film with a metal mask having 0.8 mm diameter holes. The Pt layer of the substrate acted as bottom electrode. The leakage current properties of the films were investigated using a source meter (Keithley 2612) with 0.1 V step size and 1 s delay time.

3 Results and discussion

3.1 Diffusion of the adhesion layer

To evaluate the amount of diffusion of the chemical elements of the adhesion layer into NKN SIMS depth profiles of the NKN films were recorded. The SIMS depth profiles of the NKN thin films with chromium and titanium adhesion layer with and without post-annealing treatment can be seen in Fig. 1. The NKN films are around 200 nm thick. All curves were normalised in secondary ion intensity and time. For the normalisation of the intensity the oxygen signal (not shown here) was used because as a matrix signal it exhibits a high and constant value over the whole thickness for all films. For the normalisation of the time the rise of the platinum signal was used that indicates the end

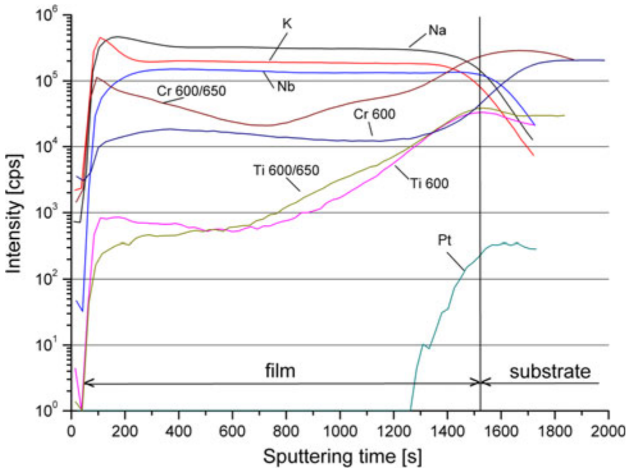

Fig. 1 SIMS depth profiles of the NKN films with Cr and Ti adhesion layer with and without post-annealing treatment

of the NKN film. The titanium curves for both samples, with and without post-annealing treatment, show a similar trend over the whole thickness. The sample with post-annealing step (Ti 600/650) shows, as expected, mostly a higher signal than the sample without post-annealing (Ti 600). The same trend is visible in Fig. 1 for the samples with chromium adhesion layer. The sample with post-annealing step (Cr 600/650) shows a higher counting rate over the whole thickness of the film. In comparison, the counting rate and the corresponding amount of the diffusion is much higher for both samples with chromium adhesion layer; even without post-annealing treatment the Cr intensity is higher than the Ti intensity. Although in general it is problematic to compare intensities in SIMS measurements, the same statement holds true if the intensities of Ti and Cr were normalized to the same end value. So it can be stated that chromium diffuses more easily into the NKN film than titanium. The platinum, on the other hand, exhibits a much steeper rising edge and thus does at most diffuse only slightly into the NKN film, as can be seen in Fig. 1. Apart from the region near the interface the counting rate of the platinum signal is close to zero inside the NKN film. Also, no variability of the sodium and potassium counting rate in the film is detectable except for the region near the surface. The alkaline elements are homogeneously distributed over the film thickness (the platinum, sodium and potassium data are exemplarily taken from the sample Ti 600/650).

3.2 Structural characterisation

The influence of the diffusion of the elements of the adhesion layer into the NKN films on the phase composition and crystal structure was investigated by XRD measurements. The XRD measurements of the NKN films with chromium and titanium adhesion layer with and without post-annealing step are presented in Fig. 2. The films with titanium adhesion layer crystallize in the perovskite single phase of NKN without any secondary phases. The NKN films were all indexed as pseudo cubic structure because no peak-split that is typical for the orthorhombic structure was visible. In contrast to the films with titanium adhesion layer the films with chromium adhesion layer are not single phase NKN because secondary phases appear, as can be seen in Fig. 2. The secondary phases are more pronounced in the film with post-annealing step (Cr 600/650). The film Cr 600 without post-annealing exhibits only very weak reflexes. The high amount of chromium diffusion seems to constrain the crystallisation process. Probably the high amount of oxygen vacancies generated to maintain the charge neutrality (see Eq. 4, Sect. 3.4) disturbs the formation of the perovskite structure. Also the replacement of Nb^{5+} by Cr^{3+} can contribute to the disruption of the lattice formation. Next to this effect, the formation of the oxygen vacancies and the replacement of Nb^{5+} by Cr^{3+} causes the appearance of the secondary phases because the stoichiometry of the NKN is not correct anymore. Probably because of the lower temperature and lower amount of chromium diffusion the secondary phases developed to a lesser extent in the film Cr 600. The appearance of the secondary phases can only be explained by the high amount of chromium diffusion into the film because this is the only difference between the films. They were prepared from the same solution with an identical temperature program. It is difficult to identify the secondary phase or phases because the reflexes are small and relatively broad but we suggest the two secondary phases are $K_8Nb_{18}O_{49}$ (ICSD 00-031-1065) and Na_4CrO_4 (ICSD 00-028-1078). There is also an effect of the chromium diffusion on the lattice parameter *a* detectable. For the film with titanium adhesion layer the lattice parameter is in both cases, with and without post-annealing treatment, $a = 3.97$ Å. This is the same value as in our former investigations [21, 22] and in good agreement with the 3.979 Å reported in ICDD card 04-007-9790. In contrast, for the NKN films with chromium adhesion layer the lattice parameter is $a = 3.93$ Å for the film without post-annealing and $a = 3.94$ Å for the film with post-annealing treatment. Tanaka et al. [10] reported $a = 3.91$ Å and concluded that the difference is caused by compressive stress from the substrate during the fabrication process. The chromium diffusion might generate lattice distortion due to the formation of oxygen vacancies to maintain the electrical neutrality. Another reason is the replacement of Cr^{3+} for Nb^{5+}. Both effects lead to stress that is responsible for the shorter lattice parameter. In the films with titanium adhesion layer the amount of titanium diffusion is much lower. As a consequence, the number of oxygen vacancies and replaced

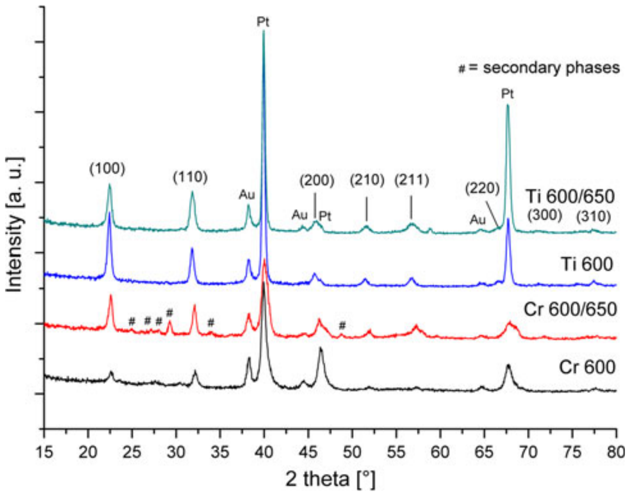

Fig. 2 XRD patterns of the NKN films with Cr and Ti adhesion layer with and without post-annealing treatment

Nb^{+5} is much lower, leading to less generated stress. Thus the lattice parameter is close to the powder value. The XRD measurements clearly indicate differences in the crystal phase as well as in the lattice parameter due to the different adhesion layers.

3.3 Morphological characterisation of the surface

To examine the influence of the different adhesion layers on the morphology of the NKN films SEM images were recorded. The SEM surface images of the films with chromium and titanium adhesion layer with and without post-annealing treatment are presented in Fig. 3. The NKN films with titanium adhesion layer are both free of pores and cracks, as can be seen in Fig. 3. For the film with post-annealing treatment Ti 600/650 the grain structure is clearly visible. In contrast, the film Ti 600 formed without post-annealing does hardly show a distinct grain structure. The films with chromium adhesion layer behave differently: both show pore formation. The film Cr 600 without post-annealing treatment has predominantly smaller pores whereas the film Cr 600/650 with post-annealing treatment exhibits larger pores. Both films have a significantly rougher surface than the films with titanium adhesion layer. The rough surface seems to be a consequence of the disturbed lattice formation because of the oxygen vacancies and replacement of Nb^{+5}, as discussed in Sect. 3.2. The grains do not grow regularly because the lattice formation is disturbed. The high amount of chromium diffusion apparently degrades the quality of the surface morphology of the NKN film. Figure 4 presents the SEM cross section images of the NKN films with chromium adhesion layer with and without post-annealing. The cross section images were taken to analyse whether or not the pores that can be seen on the surface of the films penetrate through the film. A cross section was taken of the film Cr 600 without post-annealing from a zone without pores visible in top view. No pores in the film itself are to be found. In the film Cr 600/650 with post-annealing step a cross section of a sample position with a bigger pore, see Fig. 3, was taken. The pore extends into a cavity with pore volume underneath the surface. Hence, the NKN film with chromium adhesion layer and post-annealing treatment seems to have porosity also inside of the film.

3.4 Electric properties

To evaluate the electrical properties of the NKN films leakage current measurements were performed. The results of the leakage current measurements for the NKN films with chromium and titanium adhesion layer with different heat treatments are shown in Fig. 5. The NKN films with titanium adhesion layer possess a clearly lower leakage current than the films with chromium adhesion layer. The leakage current of the films with titanium adhesion layer is 10^{-6} to 10^{-5} A/cm ^{2} at an electric field strength of 20 kV/cm. The current rises to 10^{-4} A/cm^{2} at 100 kV/cm and 10^{-3} A/cm^{2} at 200 kV/cm. Only small differences between the NKN films with titanium adhesion layer with (Ti 600/650) and without (Ti 600) post-annealing step are detectable. Maybe the higher amount of titanium diffusion seen in the SIMS measurements of the film with post-annealing treatment is compensated by differences in the electronic structure due to different oxidation states because of the post-annealing step. The values for the leakage currents of the films with titanium adhesion layer are comparable to our former investigations [21, 22]. Ahn et al. [16] and Tanaka et al. [17] found a leakage current of 10^{-6} to 10^{-5} A/cm^{2} at an electric field of 50–60 kV/cm. This is somewhat lower than the values of the films with titanium adhesion layer investigated in this study. Nakashima et al. [23] reported leakage currents for two different samples of 10^{-5} and 10^{-3} A/cm^{2}, respectively, at 150 kV/cm. The films here with titanium adhesion layer with and without post-annealing step are in between these two values at comparable field strength.

The NKN films with chromium adhesion layer have considerably higher leakage currents, as can be seen in Fig. 5. At low electric fields the leakage current is between 0.1 and 1 A/cm^{2} and rises quickly to 10 A/cm^{2} with increasing field strength. The much higher leakage currents of the NKN films with chromium adhesion layer seem to be due to the higher amount of diffusion from the adhesion layer into the film which can be seen in Fig. 1 and the pore formation, see Figs. 3 and 4. In addition to the higher amount of chromium diffusion every chromium atom generates two charges to maintain the electrical neutrality

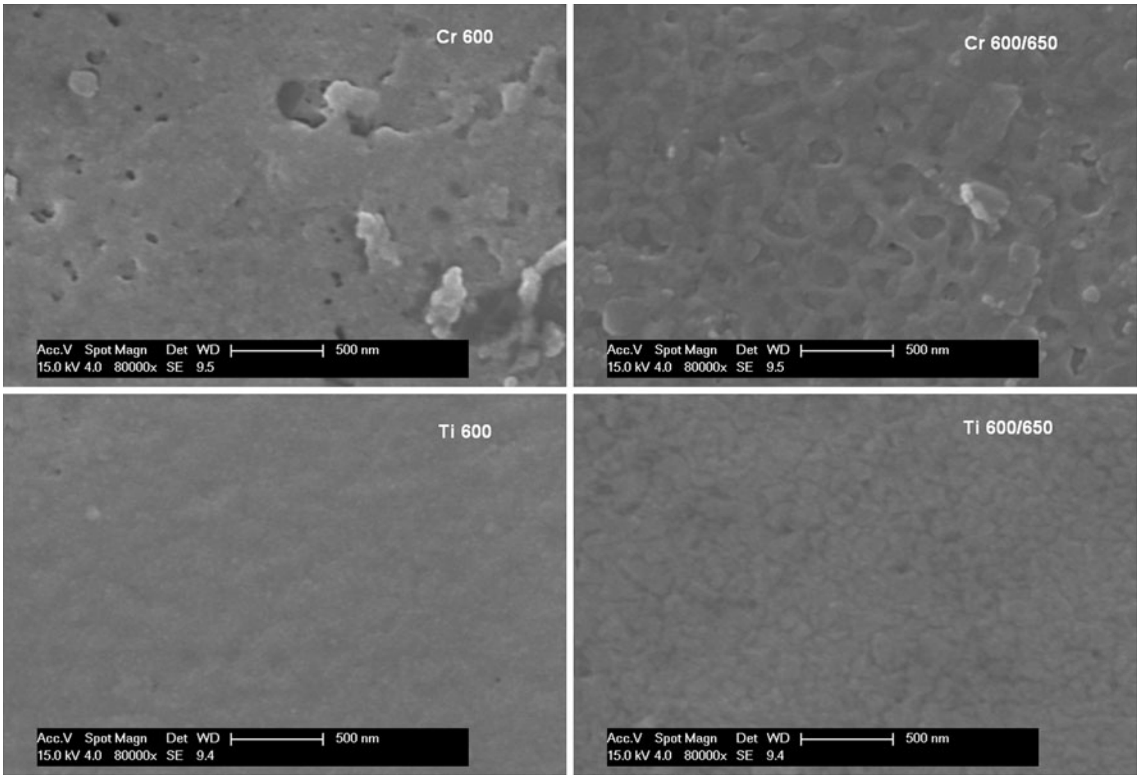

Fig. 3 SEM images of the surface of the NKN films with Cr and Ti adhesion layer with and without post-annealing treatment

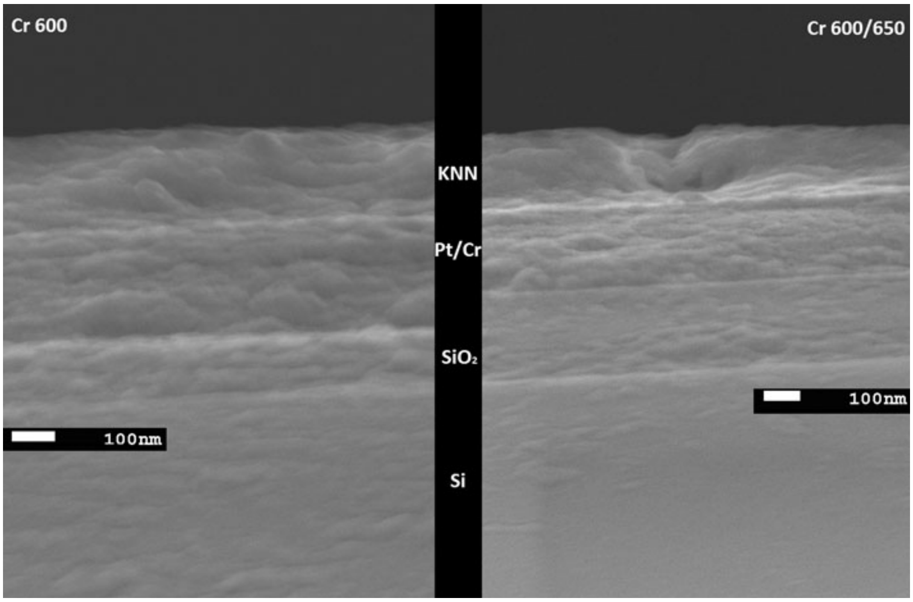

Fig. 4 Cross section SEM images of the of the NKN films with Cr adhesion layer with and without post-annealing treatment

whereas every titanium atom generates only one charge. The titanium and chromium atoms both substitute Nb^{5+} in the B-Site of the perovskite NKN lattice because of similar ionic radii (Cr^{3+} = 64 pm, Ti^{4+} = 61 pm, Nb^{5+} = 69 pm). To maintain the charge neutrality holes can be generated according to Eqs. (1) and (2) or oxygen vacancies can be formed according to Eqs. (3) and (4) or both at the same time. In both cases, holes and oxygen vacancies, the same amount of chromium diffusion generates more charges and thus a higher leakage current than the titanium diffusion. This effect together with the poor lattice formation, the formation of a secondary phase and their impact on the

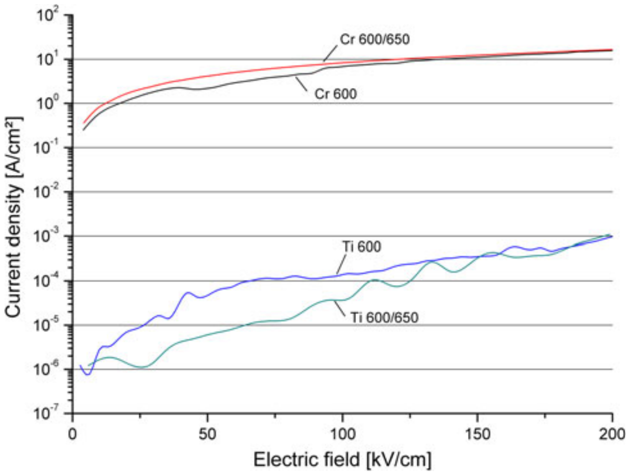

Fig. 5 Leakage current measurements of the NKN films with Cr and Ti adhesion layer with and without post-annealing treatment

surface morphology led to the high conductivity of the films with chromium adhesion layer.

$$\mathrm{Ti} \xrightarrow{b} \mathrm{Ti}'_{Nb} + h^{\cdot} \tag{1}$$

$$\mathrm{Cr} \xrightarrow{Nb} \mathrm{Ti}''_{Nb} + 2h^{\cdot} \tag{2}$$

$$2\mathrm{TiO}_2 \xrightarrow{Nb_2O_5} 2\mathrm{Ti}'_{Nb} + 4\mathrm{O}_O + V_O^{\cdot\cdot} \tag{3}$$

$$\mathrm{Cr}_2\mathrm{O}_3 \xrightarrow{Nb_2O_5} 2\mathrm{Cr}''_{Nb} + 3\mathrm{O}_O + 2V_O^{\cdot\cdot} \tag{4}$$

4 Conclusion

Adhesion layers of platinised silicon substrates exert a strong influence on the properties of sol–gel derived NKN films. SIMS depth profiles showed that although chromium and titanium both diffuse into the NKN film during heat treatment, the amount of chromium diffusion is considerably higher. For films with chromium adhesion layer extensive diffusion causes the appearance of a secondary phase and pore formation both with and without post-annealing step. The electrical properties are also degraded by the chromium diffusion. The leakage current of the films with chromium adhesion layer is about four orders of magnitude higher than for the films with titanium adhesion layer at comparable field strength. Hence, it is recommended that Cr based adhesion layers should be avoided when preparing ferroelectric thin films. In general, interdiffusion of layers seem to exert a stronger effect than expected and should be considered when NKN films are formed.

Acknowledgments The authors gratefully acknowledge the LOEWE-Zentrum AdRIA for financial support and Markus Antoni for the assistance with the synthesis.

References

1. Jaffe B, Cook WR, Jaffe JR, Jaffe H (1971) Piezoelectric ceramics. Academic Press, New York
2. Zang GZ, Wang JF, Chen HC, Su WB, Wang CM, Qi P, Ming BQ, Du J, Zheng LM, Zhang S, Shrout TR (2006) Appl Phys Lett 88:212908
3. Guo Y, Kakimoto K, Ohsato H (2005) Mater Lett 59:241
4. EU-Directive 2002/96/EC, Off J Eur Union 46 [L37] (2003) 24
5. EU-Directive 2002/95/EC, Off J Eur Union 46 [L37] (2003) 19
6. Guo Y, Kakimoto K, Ohsato H (2004) Appl Phys Lett 85:4121
7. Kizaki Y, Noguchi Y, Miyayama M (2006) Appl Phys Lett 89:142910
8. Blomqvist M, Koh JH, Khartsev S, Grishin A, Andreasson J (2002) Appl Phys Lett 81:337
9. Cho CR, Grishin A (2000) J Appl Phys 87:4439
10. Tanaka K, Kakimoto K, Ohsato H (2006) J Cryst Growth 294:209
11. Sakamoto W, Mizutani Y, Iizawa N, Yogo T, Hayashi T, Hirano S (2005) J Eur Ceram Soc 25:2305
12. Sakamoto W, Mizutani Y, Iizawa N, Yogo T, Hayashi T, Hirano S (2006) J Electroceram 17:293
13. Tashiro S, Nagamatzu H, Nagata K (2002) Jpn J Appl Phys 41:7113
14. Ahn CW, Jeong ED, Lee SY, Lee HJ, Kang SH, Kim IW (2008) Appl Phys Lett 93:212905
15. Goh PC, Yao K, Chen Z (2012) J Phys Chem C 116:15550
16. Ahn CW, Lee SY, Ullah A, Bae JS, Jeong ED, Choi JS, Park BH, Kim IW (2009) J Phys D Appl Phys 42:215304
17. Tanaka K, Kakimoto K, Ohsato H, Iijima T (2007) Jpn, J Appl Phys. 46(3A):1094
18. Goh PC, Yao K (2009) J Am Ceram Soc 92(6): 1322
19. Dai C-L, Xiao F-Y, Lee C-Y, Cheng Y-C, Chang P-Z, Chang S-H (2004) Mat Sci Eng A 384:57
20. Wang K, Yao K, Chua SJ (2005) J Appl Phys 98:013538
21. Wiegand S, Flege S, Baake O, Ensinger W. Bull Mater Sci in print. doi: 10.1007/s12034-012-0367-6
22. Wiegand S, Flege S, Baake O, Ensinger W (2012) J Mater Sci Technol 28(6):500
23. Nakashima Y, Sakamoto W, Shimura T, Yogo T (2007) Jpn J Appl Phys 46:6971