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Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and electron microprobe analysis (EMA) were applied to investigate the chemical composition, impurities, and the homogeneity of thin para- and ferroelectric epitaxial $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN) layers grown by liquid-phase epitaxy using a KTN-KF flux. AES indicated no Ta/Nb fluctuations within the layer plane and in the growth direction. XPS and EMA determined a F incorporation of 0.8–0.9 mol % for as-grown and 0.6 mol % for annealed samples. Valence analyses with XPS and electron paramagnetic resonance (EPR) revealed only the regular valence state for the B atoms of a $(I,V)\text{ABO}_3$ perovskite lattice. An unexpected splitting of the K 2p doublet peak was found for as-grown layers. Structural defects observed by optical microscopy and x-ray topography were attributed to lattice relaxation effects. Optical waveguiding could be achieved for para- and ferroelectric layers.

I. INTRODUCTION

The growth of micrometer-thick epitaxial layers of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN) for integrated optical applications require chemically homogeneous layers of high crystal quality, e.g., low optical absorption and light scattering losses. Such layers can be expected from liquid-phase epitaxy (LPE) since this process operates much closer to the chemical equilibrium as compared to other thin-film growth techniques like molecular-beam epitaxy (MBE), laser deposition, rf sputtering, etc. The restraints of the LPE method are the minimal layer thickness of about $\sim 0.5 \mu\text{m}$ and the lattice fitting between substrate and layer to reduce the defect density of the epitaxial layer. Recently, we have reported on LPE growth of KTN on cubic KTaO_3 (KT) from dilute KF solutions.^{1–3}

The leading features for the investigation of the epitaxial growth of para- and ferroelectric KTN are (i) the high dielectric permittivity near the Curie temperature,⁴ (ii) the (almost linear) composition-dependent phase transition temperatures of the KTaO_3 - KNbO_3 solid solution,⁵ and (iii) the large electro-optic and nonlinear optic effects known for KTN bulk crystals.⁴

This paper reports briefly on the epitaxial growth process, outlined in Ref. 1. In a more extensive way we shall discuss the chemical composition and homogeneity including an analysis of main impurities. Special attention will be drawn to defects arising due to a lattice misfit between the KTN layer material and the KT substrate. Finally, first optical waveguide properties are mentioned.

II. EPITAXIAL GROWTH

Epitaxial layers of KTN ($0.19 \leq x \leq 0.46$) were grown from supercooled KTN-KF solutions on KT substrates. For the determination of the necessary growth parameters

such as the range of concentration ($3 \leq c_{\text{KTN}(x)} \leq 8 \text{ mol } \%$), the supercooling ($30 \leq \Delta T \leq 100 \text{ K}$), as well as the morphological behavior for different substrate orientations, an exploratory setup (operating with several small Pt crucibles) was developed which allowed LPE experiments on a small scale, mainly assisted by an *in situ* visual observation of the dissolution and the crystallization processes.⁶

Growth on cm^2 -large (100)-oriented KT substrates was performed in a highly temperature-stabilized ($\delta T \leq 0.05 \text{ K}$) three-zone furnace. At temperatures $1150 < T \leq 1215 \text{ K}$ and growth times $1 \leq t \leq 30 \text{ min}$ growth resulted in blue-colored and electrically conductive layers with thicknesses between 2 and $45 \mu\text{m}$ (for details see Refs. 1–3). The blue color of KTN grown from KF is most probably connected with the incorporation of small amounts of F, as will be shown in Sec. III. Complete discoloration, necessary for optical and dielectric measurements, could be achieved by post-growth annealing in O_2 at 1220 K for 24 h. To avoid any out-diffusion of K_2O at temperatures $T > 1073 \text{ K}$, annealing was performed in the presence of ceramic KTN. The use of charge-compensating additives to the KF flux such as ZrO_2 or HfO_2 or pure oxide fluxes, e.g., K_2O or K_2MoO_4 , lead directly to colorless layers.

III. CHEMICAL COMPOSITION AND IMPURITIES

Preliminary analyses by means of different analytical methods showed that KTN layers obtained from pure KF solutions are epitaxially grown, optically transparent, and rather pure and homogeneous within experimental error.¹

The application of Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and electron microprobe analysis (EMA) revealed more details on the grown-in defects, the homogeneity, and on the qual-

FIG. 1. AES spectrum of an Ar^+ sputter-cleaned KTN ($x = 0.46$) layer with a thickness of $8 \mu\text{m}$, showing K, Nb, Ta, and O as the main elements.

ity of the layers. The results of these investigations will be presented in the following sections.

An Auger electron spectrum recorded on the surface of an Ar^+ -sputtered, as-grown KTN ($x = 0.46$) layer (Fig. 1) shows only K, Ta, Nb, and O as the main elements and no significant impurities. A quantitative EMA of as-grown layers from KTN [$0.68 \leq x(\text{KTN})_{\text{liq}} \leq 0.85$]-KF ($92 \leq c_{\text{KF}} \leq 97$ mol %) solutions determined layer compositions $x(\text{KTN})_{\text{sol}}$ between 0.19 and 0.46. Compared to the equilibrium distribution coefficient k_0 of the pure KTN system,⁵ the k_{eff} values for the dilute system are lower. Fluorine as the main impurity could be traced by XPS (0.8 mol %) and by EMA (0.9 mol %) for a KTN ($x = 0.29$) layer. The F $1s$ electron signal at a binding energy of 686 eV is shown in Fig. 2. Annealing of as-grown samples in an O_2 atmosphere resulted in a F decrease of 33% and a possible O increase of $\sim 1\%$ (EMA), whereas no changes in the K, Ta, and Nb concentrations could be observed. This supports the assumption that at least some parts of the F incorporation occur by substitutional replacement of O^{2-} by F^- . The charge compensation of F^- point defects could be attained by Ta^{4+} and/or Nb^{4+} on B^{5+} lattice sites of the ABO_3 perovskite lattice. However, up to now it has not been possible to detect any valence state different from B^{5+} for Ta and Nb with XPS or low-temperature EPR at 4 K. Also, no shifts of the binding energy for Ta and Nb were evident.

FIG. 2. XPS spectrum of an as-received blue-colored KTN ($x = 0.29$) layer, showing the F $1s$ peak at a binding energy of 686 eV.

FIG. 3. XPS curves (measured and fitted) exhibiting the splitting of the K $2p$ doublet peak, with $\sim 48\%$ of the intensity shifted by 1.25 eV to higher binding energies.

An unexpected result yielded XPS measurements of the binding energy of K for polished as-grown blue-colored layers: Besides the expected K $2p(3/2, 1/2)$ peak doublet (spin-orbit interaction) for KTN (see Fig. 3, doublet marked as KTN) at binding energies of 292.3 and 295.1 eV, an additional K $2p$ doublet (48% of the total K intensity) is shown at binding energies shifted by 1.25 eV to higher energies, indicating two different chemical states for the K atoms. After annealing only the K $2p$ doublet (292.3 and 295.1 eV) remained, as found for KTN. More details of the chemical nature of the shifted K $2p$ doublet (see Fig. 3) could not be determined. However, a similar chemical shift of the K $2p$ signals of 1.4 eV was reported for vacuum-annealed pure KNbO_3 .⁷ Szot *et al.* concluded that there were two different forms of K present: A more ionic K^+ and a more metalliclike form of K which contributes to the electrical conductivity. It is also known from the chemical literature that, at $p < 10^{-4}$ Torr and $T > 1073$ K, KNbO_3 decomposes into metallic K and NbO_2 .⁸ However, our measurements were only done at vacuum and room temperature.

As mentioned above, dielectric and colorless layers could also be produced directly by adding only 0.5 mol % ZrO_2 or HfO_2 to the KTN-KF solution. In this case Zr or Hf and F were significantly incorporated into the ABO_3 lattice. An EMA analysis showed, e.g., substitutional doping of nearly equivalent amounts of Zr and F ($\text{KTa}_{1-x-y/2}\text{Zr}_{y/2}\text{Nb}_{x-y/2}\text{Zr}_{y/2}\text{O}_{3-y}\text{F}_y$). Up to 50% of Nb and Ta in a KTN ($x = 0.29$) layer were replaced by Zr^{4+} . Thus, for the solution growth of KTN, KF and ZrO_2 represent an efficient diheterovalent (partial replacement of Nb^{5+} , Ta^{5+} , and O^{2-} by Zr^{4+} and F^-) substitution system. Dielectric measurements indicated that an increasing amount of Zr and F depresses T_c considerably. Zr-doped layers will hence not be useful in the present context. XPS scans of the K $2p$ spin-orbit doublet (of a KTN:Zr layer) also showed an additional doublet, indicating a second state of K with a splitting of 1.05 eV (40% of

FIG. 4. Optical micrograph (with crossed polarizers) of a KTN layer with the rectangular defect pattern oriented parallel in plane to the main cubic axes of the KT substrate.

the signal intensity) for as-grown layers, but no influence on these shifts by O_2 annealing as observed for the pure KTN layers.

IV. STRUCTURAL DEFECTS AND COMPOSITIONAL HOMOGENEITY

Any large-area and low-loss optical waveguide application of ferroelectric thin layers requires monodomain and chemically homogeneous (influence on the refractive index) material with low structural defect density. These are rather strong constraints to be fulfilled at once by a heteroepitaxial system like KTN ($mm4$)-KT ($m3m$).

In this section, we report on specific defects observed in first attempts to grow para- and ferroelectric KTN on KT. Optical microscopy (with crossed polarizers) and x-ray topography¹ revealed a distinct rectangular pattern for para- and ferroelectric layers (Fig. 4). This pattern did not influence the surface morphology, which was macrostepless for (100) substrates with a misorientation smaller than 0.5° , but it certainly decreases the optical quality, because these inhomogeneities can act as scattering areas and will influence the domain structure of ferroelectric layers in such a way that monodomain samples may never be obtained.

Let us discuss the observed defects (Fig. 4) in some detail. The rectangular pattern may be connected with structural or chemical properties of KTN and hence be caused by. (i) ferroelectric domains, (ii) lattice misfit relaxation, (iii) chemical growth inhomogeneities,⁹ and (iv) immiscibility in the subsolidus region.^{10,11}

Now, all possibilities [(i)–(iv)] will be considered successively. First, within the compositional range of $0.19 \leq x_{\text{sol}} \leq 0.46$, defects as shown in Fig. 4 were found for para- and ferroelectric layers. In the case of the paraelectric state with a T_c of, e.g., 263 K, application of a dc field up to 5

FIG. 5. KTN/KT sample as prepared for AES measurements to investigate the homogeneity of the layer on the surface, in the volume, and at the substrate/layer boundary.

kV/cm or heating up to 775 K did not induce any changes in the pattern. A strain-induced T_c shift can be excluded.¹ Therefore, it is unlikely that this pattern is produced by ferroelectric domains. Second, the fact that these defects have been observed by x-ray topography too intensifies the assumption that they are generated by lattice relaxation effects. Depending on the Nb content of the KTN layers lattice misfits f [$f = (a_l - a_s)/a_s$, where a_l , a_s are lattice constants of the layer and the substrate, respectively] in the range of $0 \leq f \leq 2.5 \times 10^{-2}$ can be expected for KT substrates.

For other materials, e.g., epitaxial layers of semiconductors, lattice relaxation effects depend critically on the layer thickness. In our case, the effect was found down to a present layer thickness minima of $\sim 2 \mu\text{m}$. A different behavior is known for the rare-earth garnet epitaxy: Because of the high energy required for the formation of dislocations, preferentially strained layers were obtained.¹² Therefore, it is not quite clear if these defects are only produced by lattice relaxation. Chemical inhomogeneities (as reported for KTN bulk growth^{4,9}) could cause similar effects.

Thirdly, to analyze the chemical homogeneity and a possible immiscibility for the subsolidus region of KTN layers, samples were prepared as shown in Fig. 5. The polishing of a $\sim 10\text{-}\mu\text{m}$ -thick layer into a wedge form of an angle of $\sim 2^\circ$ permitted a study of the homogeneity of the layer surface, the volume, and the substrate-layer interface in one step without sputtering during the measurement or grinding the layer in between. This sample preparation will also increase the depth resolution. The present investigations are of particular importance for optical applications because any considerable variation in the Nb/Ta concentration ratio would locally change the refractive index tensor. Further on, the Nb gradient at the substrate-layer interface is defining the barrier geometry and hence the optical confinement of the waveguides.

All homogeneity measurements were performed by AES. AES provides a qualitative determination of the deviation of K, Ta, Nb, and O with respect to a KTN reference with an accuracy of $\pm 3\%$. (The accuracy in absolute concentration, using the elemental cross section, is about 25%.) One has also to keep in mind that chemical changes influence the AES peak shapes and generate changes of up to 20%. Such a typical AES effect can be seen in Fig. 6,

FIG. 6. AES line scan recorded on a wedge-polished KTN ($x = 0.46$) sample (prepared as shown in Fig. 5) with profile A parallel to (a), profile B parallel and near the substrate/layer boundary, and profile C in the diagonal direction as (c). No correlated Nb/Ta variations could be observed. The sharp intensity loss in profile A at $\sim 500 \mu\text{m}$ was caused by a dust particle.

profile A, where, due to an increase of the Nb content at the interface, the intensities for K and O decrease/increase, respectively. The high lateral resolution of the available spectrometer of $\sim 0.5 \mu\text{m}$ is sufficient for the investigation of the observed pattern (Fig. 4) with an average periodicity of $\sim 1\text{--}5 \mu\text{m}$. Qualitative line scans in different directions were done as indicated in Fig. 5 and the results are displayed in Fig. 6. From all quantitative measurements on this sample one can say that constant Nb/Ta ratios were observed within an experimental error of 1%, both in the layer plane and perpendicular to it. Furthermore, the substrate-layer boundary is quite sharp and exhibits no interdiffusion. Therefore, a steplike refractive index profile can be expected for waveguides. In Fig. 6 line scans for dif-

FIG. 7. Intensity distribution of a guided He-Ne laser light beam (horizontal stripe) in a $16\text{-}\mu\text{m}$ -thick KTN ($x = 0.19$) layer.

ferent directions are shown: (A) line scan perpendicular to the substrate-layer boundary [parallel to (a) in Fig. 5] mapping the depth profile of the layer from the substrate to the layer surface, (B) parallel to the layer boundary, and (C) diagonal to directions in (A) and (B). Qualitative and quantitative measurements are consistent and bear no evidence of Nb/Ta fluctuations within experimental error. A quantitative determination of the Nb content also agrees with earlier analytical results gained by EMA, SIMS, and dielectric T_c measurements.¹ A qualitative element mapping over a $360 \times 500 \mu\text{m}^2$ area indicated no fluctuations in the Nb/Ta ratio. We can say that KTN layers investigated by AES are homogeneous both within the layer plane and in the growth direction. Therefore, the last two possibilities as an origin of the described defect pattern can be excluded. This motivated us to concentrate our future work on the second point: the misfit relaxation induced by the large difference in the lattice constants ($5 \times 10^{-3} \text{\AA}$ for $x = 0.29$) and its reduction by appropriate doping of the substrate or the layer.

V. OPTICAL WAVEGUIDING

First waveguiding experiments using a He-Ne laser light source were performed for para- and ferroelectric KTN layers. Due to the defects described above, only weak guided beam intensities can be expected. However, a guided beam could be observed by focusing the laser beam with a microscopic objective ($63\times$) on the polished end face of a cubic $16\text{-}\mu\text{m}$ -thick and 10-mm -long KTN ($x = 0.19$) layer. The guided light beam was (at the other end of the layer) magnified with a second microscope objective ($40\times$) and projected on a screen. A picture of the projection is shown in Fig. 7. Also dark- and brightline spectra could be seen for a ferroelectric layer by means of the prism coupling method. Because of high scattering losses only a few and faint brightlines were observed so far.

VI. ANALYTICAL EQUIPMENT

For the AES measurements a Perkin Elmer PHI-4300 high-resolution scanning Auger system was used. The analysis was performed at a primary electron-beam voltage of 5 kV and at a typical beam current of 330 nA. The cylinder mirror analyzer (CMA) was operated at 0.6% resolution and the channeltron electron counter was in the V/F (voltage/frequency) mode. The cleaning of the samples was done by Ar^+ sputtering at 4.5 kV over a $5 \times 5 \text{ mm}^2$ rectangular area. Line scans and maps have been recorded in the normalized three-point method (signal height/background intensity) to correct for topographical effects.¹³

The photoelectron spectroscopy measurements were done with a Perkin Elmer PHI-5400 small-spot XPS equipped with a channel plate and Mg x-ray source operated at 400 W and 15 kV. The spectrometer was calibrated with Cu (2p) and Au (4d, 4f) standards with an accuracy of $\pm 0.2 \text{ eV}$. Curve fitting was carried out by a least-squares p -doublet fitting procedure.

All measurements were done at room temperature and a base pressure of $5 \times 10^{-10} \text{ mbar}$ for both systems.

The EMA investigations were performed with a Cam-eca SX 50 system using a Sun microsystems workstation. Before measurements all samples were polished and covered with $\sim 20 \text{ nm}$ carbon. The analyses were done with a beam voltage of 15 kV and a beam current of 20 nA. As references, KNbO_3 , KTaO_3 , and LiF were used.

The EPR spectra were recorded on a Varian E-109 X-band spectrometer. For the measurement of the magnetic field and the frequency a Varian NMR Gaussmeter and a EIR 350 D counter were used, respectively. All EPR measurements were performed at 4 K. Low temperature was achieved by an EPR-10 helium flow cryostat and controlled with an Oxford VC 30 instrument.

VII. DISCUSSION AND CONCLUSIONS

Epitaxial micrometer-thin layers of KTN grown from a dilute KF flux were found to be chemically homogeneous (AES, EMA). The main impurity is fluorine with a concentration of less than 1 mol % (XPS, EMA). Post-growth annealing in O_2 resulted in a complete discoloration and conversion of blue and electrically conductive as-grown layers into dielectric samples, accompanied by a reduction in the F content by $\sim 33\%$.

The fluorine incorporation, the intense and broad IR absorption, and the electrical conductivity raise the question of a possible mechanism for the formation of defects, such as color centers, during growth. From visual inspection of the epitaxial crystallization on KT, we know⁶ that KTN layers grown from KF solutions are blue from the earliest stages of growth. Hence, in our case two chemically different forms of potassium are obviously present in the layer (the generation of one chemical state near the surface by polishing is unlikely, but cannot be excluded), since all samples appear to be homogeneously colored. Earlier, Matthias and Remeika¹⁴ assumed that the dark blue color was caused by the formation of some amounts of

Nb_2O_4 . However, the situation seems to be much more complicated. In the following sequence of arguments we try to give an interpretation consistent with all we have observed.

The charge compensation for small amounts of F^- by Nb^{4+} and/or Ta^{4+} can most probably be excluded because ESCA and EPR ($T \leq 4 \text{ K}$) could not detect valence states other than B^{5+} for the ABO_3 lattice. Instead of an effect on the B site the splitting of the K 2p spin-orbit doublet revealed two energetically different K binding states for the A site. After annealing in an O_2 and K_2O atmosphere only a single K 2p doublet at binding energies of 292.3 and 295.1 eV remained, the color, the conductivity, and some F disappeared. Is the F^- incorporation a necessary prerequisite to produce the color centers? It was stated¹⁵ that small F^- contents in the melt of pure KNbO_3 can lead to blue-colored bulk crystals. Also it was claimed that as-grown pure KNbO_3 single crystals can show different color effects, leading to blue samples, that are attributed to color centers as detected by positron annihilation.¹⁵ On the contrary, Varnhorst *et al.*¹⁶ attributed some blue-color effects of as-grown KNbO_3 to light scattering phenomena.

In our case the addition of only 0.5 mol % ZrO_2 to the KTN-KF flux resulted in colorless as-grown but heavily Zr- and F-doped layers or small crystals ($\text{KTa}_{0.62}\text{Nb}_{0.19}\text{Zr}_{0.19}\text{F}_{0.21}\text{O}_{2.79}$). Surprisingly these layers also showed a splitting of the K 2p peaks with 40% of the intensity shifted by 1.05 eV. However, an annealing process as applied for the discoloration of the blue-colored KTN layer grown from a KTN-KF flux did not influence the splitting.

The charge compensation for F^- by Zr^{4+} behaves totally differently for the pure KTN-KF flux, where blue layers or crystals were obtained for any growth conditions (fast or slow growth rates and various KTN-KF flux conditions). F^- is therefore not considered to be the primary and only cause for the observed blue color and the electrical conductivity. As a further important note, we should add here that a rocking curve analysis¹ on as-grown blue samples showed only a FWHM of 268 s compared to the substrate with 114 s. Also electron channeling and 2θ x-ray measurements confirm a cubic ($x = 0.29$) structure. The described defects do not evidently influence the crystal structure of the KTN layers.

As a possible answer to the fact that K_2O or K_2MoO_4 fluxes gave exclusively colorless layers, we assume that the chemically reductive nature of the KF media as well as small F^- doping need charge compensation for missing O^{2-} ions. These O^{2-} vacancies may lead to blue-colored layers and may also be responsible for the splitting of the K 2p binding energy for KTN samples (in the bulk or near the layer surface) grown from pure KF solutions. LPE from fluxes containing 5 mol % KF and 90 mol % K_2MoO_4 gave almost colorless layers.

Main features found earlier for vacuum-annealed KNbO_3 are similar to what we report here. However, the electronic structure of the unexpected "metallic"-like K binding state will need further investigation.

Concerning the structural defects, AES and EMA showed no Nb/Ta variation for the KTN layers. Therefore, we consider these defects (shown in Fig. 4) as lattice relaxations due to a lattice misfit f in the range of $f = 1.25 \times 10^{-3}$ for micrometer-thick layers. For future optical applications it will be necessary to avoid these defects either by growing layers with thicknesses below a critical value or by reducing the lattice misfit by appropriate doping of the substrate or the layer. Also the problems related to the formation of ferroelectric domains and poling may only be successfully solved if such a high dislocation density near the substrate layer boundary is absent.

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