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The influence of barrier layers (SiO_2, Al_2O_3, W) on the phase formation and stability of RuAl thin films on LGS and CTGS substrates for surface acoustic wave technology

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ABSTRACT

In order to achieve a higher thermal stability of RuAl thin films on LGS ($La_3Ga_5SiO_{14}$) and CTGS ($Ca_3TaGa_3Si_2O_{14}$) substrates and to prevent an oxidation with Oxygen originating from the substrates various barrier layers (SiO_2, Al_2O_3, W) are tested. The RuAl-barrier films were annealed at 800 °C for 10 h under high vacuum conditions. An analysis of the phase formation as well as of changes in the chemical composition of the RuAl film and the substrate reveals a strong dependence of the quality of the RuAl film on the applied barrier layer. In the case of Al_2O_3 a reaction between RuAl and the substrates takes place. The application of W films is challenging because of the high stresses which are present in the layer stack. However, SiO_2 films act successfully as diffusion barriers.

1. Introduction

The growing interest in surface acoustic wave (SAW) based sensors operating at higher temperatures led to an increased research on the topic of high temperature stable substrates and metallizations during the last years. Among others, promising candidates for high temperature applicable substrates are the piezoelectric crystals LGS ($La_3Ga_5SiO_{14}$) and CTGS ($Ca_3TaGa_3Si_2O_{14}$) [1,2]. A variety of possible metallizations has been considered until now, e.g. Pt [1,3], Pd [1], Ir [4] or Ir/Rh [5]. Also RuAl has been discussed as a potentially suitable metallization because of its outstanding high-temperature properties [6–9]. It is known that the application of LGS and CTGS is challenging due to a diffusion of Ga and O out of the substrate during heat treatments, especially under vacuum conditions [10–13]. Former investigations showed a strong reaction between the RuAl metallization and LGS as well as CTGS substrates [14]. On LGS, after heat treatment at 800 °C under vacuum conditions there is a complete decomposition of the RuAl layer into a thick Al_2O_3 layer on top of the substrate and a pure Ru layer above it. Al is less oxidized on CTGS so that a small amount of the RuAl phase is still present after annealing at such a high temperature. In contrast to these substrates, on thermally oxidized Si substrates, the RuAl was stable after an 800 °C heat treatment [9]. In the prior, not only the metallization was affected by the heat treatments, but cross section analyses also revealed huge inhomogeneities at the LGS and CTGS substrate surface. For CTGS, a 100–150 nm thick disturbed layer with huge variations in composition was observed in the substrate immediately below the interface to the film, while on LGS changes are only found at discrete positions; however, they reach several 100 nm into the substrate.

The reaction between film and substrate depends on the deposited material. Aubert et al. reported the complete oxidation of an Ir metallization on LGS after high temperature vacuum annealing [4]. Our studies on W films deposited on CTGS exhibited a high stability of the films up to 800 °C [15]. No chemical reaction between the film and substrate was observed and the phase purity of the film was retained. On LGS, the W film was degraded at several locations forming blister-like features on the surface. These blisters originated in the substrate due to the outflow of the substrate material and are expanded through the W film. However, the W film was not oxidized at these locations. Additionally, at the non-defected areas on the film surface, the purity of the W film was maintained. Thus W was found to be chemically stable on LGS.

These findings lead to the attempt to include barrier layers for

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RuAl films on LGS and CTGS substrates to prevent diffusion of O and Ga out of the substrate and therefore to stabilize both the substrate and the metallization. Of course it has to be considered that any interlayers will slightly influence the SAW generation as well as propagation depending on their acoustical and electrical material properties (i.e. elastic stiffness constants, density, dielectric constant and conductivity). Especially, nonconductive barrier layers affect the efficiency of electro-mechanical coupling that is partially reduced by a thin dielectric layer because of absence of a low resistance ohmic dc contact. However, those electrical effects can be considered in simulation and design of the SAW structures. In case of conductive barrier and cover layers only the finger electrodes themselves are surrounded by a thin layer. The gaps in between different electrodes remain uncovered to prevent short-circuits and electric shunt effects.

Mouzolf et al. already suggested Al_2O_3 as barrier layer for Rh/ZrO_2 or PtRh/HfO_2 films on LGS [16]. They found that atomic layer deposited Al_2O_3 leads to better stability of Pt–Rh/HfO_2 films heated in air at 1050 °C for 4 h. They assume that it acts as a diffusion barrier for substrate atoms, so that the formation of less stable phases is reduced.

A barrier layer needs to fit to both the substrate as well as to the metallization. On the basis of the mentioned experimental results, three barrier layers have been chosen for the LGS/CTGS–RuAl system: SiO_2, Al_2O_3 and W. In this paper we discuss the influence of the barrier layer on the phase formation and phase stability of the RuAl phase after annealing the system at 800 °C under high vacuum conditions. Besides this, the stability of the substrates will be analyzed. Especially, transmission electron microscopy is applied to investigate whether chemical changes have taken place within the substrate and the RuAl film.

2. Experimental

All films were deposited by sputtering in a high-vacuum chamber. RuAl was prepared at room temperature by DC co-sputtering with a thickness of 110 nm. The barrier layers SiO_2 and Al_2O_3 have been RF-sputtered from oxide targets. The deposition temperature for SiO_2 was 180 °C and for Al_2O_3 100 °C. In the case of SiO_2 the sputtering gas was a mixture of Ar and O_2 with the ratio 6:1.

In the case of W one has to take into account that there exists a stable α- (bcc) and an unstable β-phase (A15 structure, cubic). Which phase is formed during deposition depends on various conditions like film thickness and temperature [17–19].

Two sets of samples with W barrier are prepared - one with W deposited at room temperature, the other with a W deposition temperature of 400 °C since the irreversible phase transition from β-W to α-W is assumed to be caused - among others - by a heat treatment at temperatures higher than 400 K [19]. In the following, the W films deposited at room temperature (RT) are denoted as W_{RT} and those prepared at 400 °C as W_{400}.

For each barrier material, two sets of samples with 10 and 100 nm thickness of the barrier layer have been prepared. An overview of the investigated samples is presented in Table 1.

After preparation, the samples were annealed under high vacuum conditions ($p<10^{-5}$ mbar) at 800 °C for 10 h. Phase formation was analyzed by X-ray diffraction in Bragg-Brentano geometry (XRD, Philips X'Pert PW3040/00, Co-Kα) and the texture was determined via pole figure measurement (Philips XPert, Cu Kα). The film morphology was investigated by scanning electron microscopy (SEM, Zeiss Ultra Plus) and atomic force microscopy (AFM, AFM Dimension Icon Bruker Nano GmbH). Cross sections of the samples were prepared by the in-situ lift out technique in a focused ion beam microscope (FIB, Zeiss 1540 XB CrossBeam using Ga^+ ion milling). For the chemical analysis Auger electron spectroscopy was applied (AES, JEOL JAMP-9500F Field Emission Auger Microprobe). Depth profiles are measured by sputtering with Ar ions for 60 s with an ion energy of 1 keV and a current of 0.7×10^{-6} A (corresponding to a removal rate of 6.6 nm/min of SiO_2).

Table 1
Overview of the applied substrates, barrier layer materials and their thicknesses.

Substrates	LGS and CTGS
Barrier layers	SiO_2, Al_2O_3, W_{RT}, W_{400}
Barrier layer thickness	10 nm and 100 nm
RuAl film thickness	110 nm

Transmission electron microscopy (TEM, FEI Technai F30) in high-angle annular dark field scanning mode (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) on FIB prepared TEM lamellae were used to image the microstructure and to reveal local changes of the composition of the film and the substrate. All measurements were performed at RT.

3. Results

3.1. Barrier layers on LGS

3.1.1. Phase formation

The XRD measurements of the samples prepared on LGS with the different barrier layers are summarized in Fig. 1. Quantitative analyses and interpretation have to be evaluated very carefully, since only one reflex (RuAl (100)) is visible for the samples and differences in its height might not only be caused by a difference in the degree of crystallinity but also by differences in texture and chemical inhomogeneities. Nevertheless, the XRD results give an idea about the phase formation and preferred texture and have to be evaluated together with the results of the other measurement techniques.

Clearly visible is the dependence of the measured RuAl peak intensity on the applied barrier layer, which might be caused by different effects like surface energies and atomic order at the surface of the barrier layer which acts as a starting point for the growth of the RuAl phase.

Nearly for all films only the RuAl (100) crystal orientation appears except for the 100 nm W_{RT} film where a high RuAl (110) reflex is detected. At RT (Fig. 1 (a)), the highest intensity of the RuAl (100) peak is reached for the 100 nm Al_2O_3 layer.

After annealing at 800 °C the RuAl reflexes shift to higher angles (Fig. 1(b)), which might be caused e.g. by tensile stresses in the film or by a change in composition of the RuAl-phase due to the reduction of the Al content because of the oxidation of Al (see Sec. 3.1.3). The RuAl (100) peak intensity significantly increases for the 10 nm W_{RT} barrier and slightly for the 100 nm W_{400} and both 10 and 100 nm SiO_2 barrier layers. For the 100 nm W_{RT} barrier the RuAl (100) reflex disappears completely and the RuAl (110) reflex becomes more pronounced. The peak intensity of the RuAl deposited on 100 nm Al_2O_3 decreases while for the 10 nm Al_2O_3 film no RuAl reflex is left. A formation of Ru reflexes is observed after annealing, which is most dominant for the 10 nm Al_2O_3 barrier layer.

After preparation, the measurement of both 100 nm thick W films shows a strong reflex at $2\theta=46.8°$, which can be ascribed to the (210) reflex of β-W phase. The shoulder at about 47.2° matches with the α-W (110) reflex. Although this XRD peak doesn't show a large difference between the W_{RT} and W_{400} film, the influence on the RuAl phase is strong: the deposition of W at RT leads to a strong RuAl (110) reflex while the W deposition at 400 °C results in a RuAl (100) orientation.