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Multilayer structures of silicon-suboxide embedded in single crystal silicon

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Si/SiO_x multilayer structures with ultra-thin silicon-suboxide layers are fabricated with molecular beam epitaxy. The silicon surface is oxidized during growth interruptions at an oxygen pressure between 1.0×10^{-7} mbar and 8.0×10^{-7} mbar. Overgrowth with Si of the oxidized surface is possible for coverages of a few monolayers of O and improves with increasing substrate temperature. X-ray diffraction shows that the silicon layers are single crystalline. Transmission electron microscopy measurements show that the suboxide layers are ~ 1 nm thick, pseudomorph, and exhibit crystalline order throughout the layer. In addition, transmission electron microscopy shows that the oxygen concentration is laterally inhomogeneous. The multilayer structures are thermally very stable, as rapid thermal annealing up to 1000 °C shows no influence on the X-ray diffraction patterns.

1. Introduction

The silicon–silicondioxide interface plays an important role in semiconductor technology and has been studied for a long time. The presence of silicon–suboxide (SiO_x) at the interface has been shown by several groups [1–9]. Interest in the presence and properties of SiO_x are not only of academic nature, a better understanding of the formation and structure of the Si–SiO_2interface could help to improve thin metal-oxide-semiconductor (MOS) structures. Furthermore, SiO_x layers embedded in single crystalline silicon (c-Si) could be a way to improve the thermoelectric properties of Si because thin SiO_x layers are expected to reduce thermal conductivity but still enable high electrical conductivity and therefore satisfy the need for cheap and abundantly available material for high temperature thermoelectric materials.

Silicon-suboxide has almost exclusively been studied at the interface of Si/SiO_2 structures. The atomic structure and the crystalline form of SiO_x is controversial. In order to explain the Si/SiO_2 interface crystalline structures several groups have discussed various models for the interface such as tridymite [10,11], cristobalite [12] or quartz [10] as well as non-crystalline structures such as bridge-bonded network structures [13].

Wei et al. have shown that areas in a SiO_2 layer not overgrown with SiO_2 can serve as seed for subsequent crystalline silicon overgrowth [14]. Studies to produce a SiO_x tunnel barrier in Si by Sticht et al. showed that a SiO_x layer can be overgrown with crystalline Si [15]. In this study we first present a method to grow multilayer-structures of pseudomorph, single crystalline Si and SiO_x layers with up to 20 repetitions. Second, we present that the oxygen content can be analyzed with X-ray diffraction combined with simulations.

2. Experimental techniques and growth

Preparation and growth of the samples are performed in a Riber32 molecular beam epitaxy (MBE) chamber with a base pressure $< 1 \times 10^{-10}$ mbar. The MBE reactor is modified to accommodate a Si electron beam evaporator and features a pneumatic leak valve for O_2inlet in the range of 1×10^{-9} mbar to 5×10^{-5} mbar. Silicon(100) wafers, boron-doped, with high (> 10000 Ωcm) and low (< 0.02 Ωcm) resistivity are used as substrates for the growth. Typical Si growth rate of this MBE reactor is 0.15 Å/s. The substrate temperature (T_{sub}) is measured by means of a thermocouple behind the substrate heater. The substrate temperature is controlled by a PID

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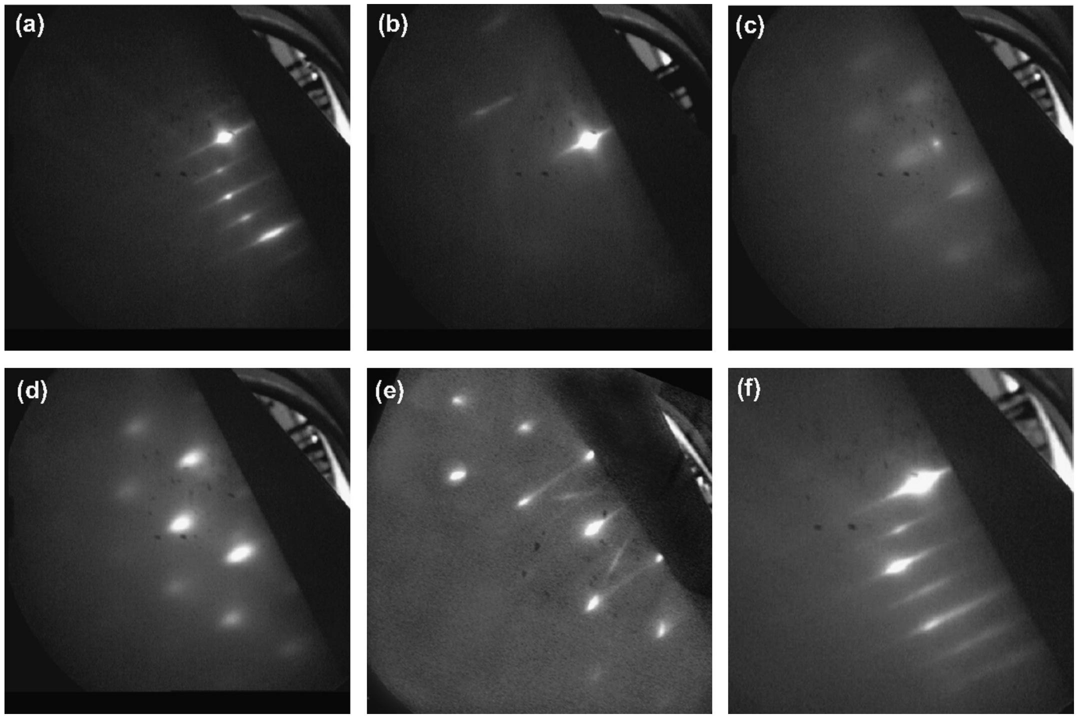

Fig. 1. RHEED images during Si/SiO_x layer growth. In (a) the clean and flat 2×1 reconstruction of the silicon buffer layer is visible, (b) 15 s into the SiO_x layer growth, the pattern is hardly visible anymore. The images (c), (d) and (e) were taken 6 ML, 10 ML and 66 ML, respectively, of Si growth after the oxygen valve was closed. Image (f) shows the surface reconstruction after 40 nm silicon layer growth. Spotty features are replaced by streaks from a smooth 2×1 silicon reconstruction.

controller and the reproducibility of T_{sub} between the samples is very high although there exists an undetermined offset to the actual sample surface temperature. Oxygen inlet is measured by means of a Bayard–Alpert type pressure gauge. The pressure is taken 30 s after opening the leak valve.

The growth process is monitored by reflection high energy electron diffraction (RHEED). Fig. 1 shows an image sequence of the growth and Si overgrowth of a SiO_x layer. In Fig. 1(a) the 2×1 reconstruction of the Si(100) surface is shown. When the Si growth is stopped and the O_2 valve opened, the RHEED pattern disappears indicating an amorphous surface (Fig. 1(b)). Between closing the O_2 valve and resuming Si growth, we introduced a 10 s process break to eliminate excess O_2 in the growth chamber and ensure a low background pressure for growth ($< 2.0 \times 10^{-8}$ mbar). After deposition of nominally ~ 6 monolayers (ML) of Si the diffuse RHEED is replaced by a transmission diffraction pattern indicating a rough surface (Fig. 1(c)). The diffraction spots become more pronounced during the deposition of the next 5 ML (Fig. 1(d)). During deposition of about 66 ML the pattern gradually changes and streaks develop indicating a flattening of the surface (Fig. 1(e)). Fig. 1(f) shows the surface after 40 nm of Si deposition, the visible Si 2×1 reconstruction is evidence for a predominantly two-dimensional crystalline silicon layer. The RHEED observations suggest that, after the Si surface has been exposed to oxygen, the Si overgrowth starts in a kind of island-growth-mode. This is in agreement with the observations of Wei et al. and Barski et al. of the overgrowth process [14,16]. In the course of the Si overgrowth the surface smoothens out and the two-dimensional Si 2×1 is restored.

In order to measure the surface roughness directly, we stopped the growth of some samples at different stages of overgrowth and analyzed the surface with atomic force microscopy (AFM). Fig. 2 shows 2.5 μm × 2.5 μm AFM scans of a SiO_x layer after overgrowth by Si with nominal thickness of (a) 3.2 nm, (b) 24 nm and (c) 35 nm. Fig. 2(a) corresponds to the growth phase in which the RHEED shows a 3D pattern, islands of about 2 nm height and 25 nm width are observed. With increasing Si layer thickness larger islands develop, see Fig. 2(b). In this stage the RHEED shows a mixture of 2D and 3D pattern. The islands increase laterally to form large Si plateaus separated by trenches (Fig. 2(c)). Further overgrowth produces a smooth Si surface within measuring limits of AFM with a typical Si(100)-2×1 surface reconstruction visible with RHEED. Fig. 2(d) shows the recovered flat surface of a $5 \times$ Si/SiO_x multilayer structure, the Si layer thickness is 48 nm. The surface shows roughness comparable to a Si buffer layer grown with MBE. For multilayer structures the Si layer thickness is chosen to be sufficiently thick in order to produce a flat Si surface before the next SiO_x layer is grown.

The Si overgrowth and the smoothing of the surface are strongly influenced by the substrate temperature. For 550 °C $< T_{sub} <$ 600 °C we observe that the smoothing process needs at least 50 nm Si overgrowth, whereas for 620 °C $< T_{sub} <$ 700 °C the smoothing process takes only for about 30 nm. The higher T_{sub} increases the surface mobility of the Si atoms and therefore enhances the smoothing process. Furthermore, at higher T_{sub} more SiO desorbs from the Si surface [17] particularly from sites not entirely covered with Si and thus reduces the amount of oxygen incorporated in the SiO_x layer. Subsequently, the surface roughness is reduced and the sample becomes more smooth. To avoid oxygen desorbing in the form of SiO at high temperatures, we introduced T_{sub} ramps into the growth process. The Si surface is oxidized at T_{sub} = 550 °C. When Si growth is resumed, T_{sub} is constantly raised to the desired Si growth temperature at a nominal rate of 0.5 °C/s.

The relatively low growth rate limited the maximum numbers of repetitions of the Si/SiO_x multilayer structures to 20. RHEED and XRD did not show a degradation of structural quality compared to the multilayer structures with 5 repetitions presented in the following.

3. Characterization with TEM and SIMS

The images in Fig. 3 show one of the SiO_x layers of a $5 \times$ (73 nm Si/SiO_x) multilayer structure. In the bright-field (BF) TEM image