Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 6332 – 6336
thin solid films
www.elsevier.com/locate/tsf

Hetero-epitaxy of $SrTiO_3$ on Si and control of the interface

G. Delhaye *, M. El Kazzi, M. Gendry, G. Hollinger, Y. Robach

LEOM, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, 69134 Ecully, France

Available online 24 January 2007

Abstract

In this article, we address some critical issues to the hetero-epitaxial growth of $SrTiO_3$ on Si, with emphasis on the interface properties. A two-step growth process allows us to obtain oxide films with high crystallinity, and prevent the formation of an amorphous silicon oxide at the interface. The chemical and structural properties of the interface were evaluated using reflection high energy electron diffraction and X-ray photoelectron spectroscopy. Conditions of hetero-epitaxial growth were first calibrated by a preliminary study of the homo-epitaxial growth of $SrTiO_3$.

Keywords: Molecular beam epitaxy; $SrTiO_3$; Integration on Si

1. Introduction

Despite its difficulty, the integration of epitaxial crystalline oxides on silicon has been widely investigated for several years [1–4]. If a first motivation was to replace the amorphous SiO_2 gate dielectric in silicon-based metal-oxide-semiconductor fields effect transistors, nowadays another goal is the integration of new ferroelectric, magnetic, or optoelectronic functionalities on Si. Among the studied crystalline oxides, $SrTiO_3$ has been recognized as a promising candidate [5,6]. Its direct epitaxy on Si has been achieved with a high degree of crystallinity, a low density of interface defects, under low temperature and low oxygen pressure conditions that allow to minimize the formation of an interfacial SiO_2 oxide. To create epitaxial structures in which the properties of both the underlying silicon and overlying oxide are preserved, the control of the silicon — crystalline oxide interface is essential. The properties of the interface such as stability against interfacial reactions, strain relaxation or silicon oxidation will determine the functionality of the epitaxial structures.

In this work, we present results on the hetero-epitaxial growth of $SrTiO_3$ on Si by molecular beam epitaxy (MBE) by a two-step growth technique. The MBE technique is used for its superior capability in atomic level interface engineering and control. Different ways of elaboration are compared and the influence of technological parameters such as substrate temperature is studied, with emphasis placed on obtaining a sharp interface. Preliminary results on the homo-epitaxial growth of $SrTiO_3$ on $SrTiO_3$ are also presented as a calibration tool.

2. Experimental procedure

The growth of $SrTiO_3$ epitaxial layers was performed in a RIBER EVA 32 MBE reactor, with a base pressure better than 5.3×10^{-8} Pa. Sr and Ti metals were co-deposited by thermal evaporation of respectively low and high temperature effusion cells; molecular oxygen was introduced into the chamber through a needle valve. Calibration of the fluxes was done with a quartz crystal microbalance and in-situ reflection high energy electron diffraction (RHEED) was used to probe the film surface during growth. Additional information was obtained ex-situ by X-ray photoelectron spectroscopy (XPS), chemical information, and atomic force microscopy (AFM), topographical information.

For the homo-epitaxial growth, $SrTiO_3$(001) substrates were etched in a buffered HF/NH_4F solution, leading to a clean TiO_2 terminated surface, and then annealed under oxygen at 1.3×10^{-4} Pa and a substrate temperature of 923 K or 1023 K. Prior to the hetero-epitaxial growth, the Si(001) substrates were submitted to an ultraviolet (UV)-ozone treatment to remove

* Corresponding author.
E-mail addresses: Gabriel.Delhaye@ec-lyon.fr (G. Delhaye), Mario.Kazzi@ec-lyon.fr (M. El Kazzi), Michel.Gendry@ec-lyon.fr (M. Gendry), Guy.Hollinger@ec-lyon.fr (G. Hollinger), Yves.Robach@ec-lyon.fr (Y. Robach).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.11.187

carbon contamination and etched in a diluted HF solution. A subsequent UV-ozone treatment allowed the formation of a well controlled native oxide. An initial SiO_2 free silicon surface was obtained trough a strontium-induced de-oxidation process [7,8]. This was accomplished by depositing approximately two monolayers (MLs) of Sr metal on the Si surface at approximately 873 K and followed by heating up the Si sample to 1073 K and remaining at that temperature for at least 20 min. This process led to a stable sub-monolayer silicide structure. A small amount of Sr was then added to the surface at 873 K to form a clean (2×1) reconstruction characteristic of a ½ ML Sr coverage.

3. Results and discussion

3.1. Homo-epitaxial growth of $SrTiO_3$ on $SrTiO_3$

Homo-epitaxial $SrTiO_3$ thin films were deposited at different deposition rates and substrate temperature. After etching and introduction in the UHV chamber the substrate was annealed at 923 K or 1023 K for 1 h. Before the homo-epitaxial growth, the RHEED pattern (Fig. 1) shows a 2×2 reconstruction characteristic of a Ti-rich or TiO_2-terminated $SrTiO_3$ surface [8]. This reconstruction is less pronounced at 923 K but a good crystalline quality is observed in the two cases.

The homo-epitaxial growth of $SrTiO_3$ was initiated at approximately 1.3×10^{-4} Pa of partial pressure of molecular oxygen and studied as a function of substrate temperature between 523 K and 1023 K. Results are illustrated in Fig. 2 which show the RHEED specular spot intensity for 3 characteristic temperatures: Above 723 K, many oscillations are observed, attesting a good two-dimensional growth and the RHEED pattern at the end of the growth shows a high crystalline quality. At smaller temperatures, the 2D growth is limited and evolution towards roughening and 3D growth occurs. AFM images acquired ex-situ at the end of the growth also clearly reveal at higher temperatures a well defined step terrace morphology (Fig. 3). Comparatively, in the studied range, the growth rate seems to have no influence.

3.2. Hetero-epitaxial growth of $SrTiO_3$ on Si

Direct epitaxy of a $SrTiO_3$ on Si was not successful: Whatever the growth temperature, an amorphous $SrTiO_3$ layer was grown. Crystalline growth was only obtained by a two-step growth technique as follows: In a first step an amorphous

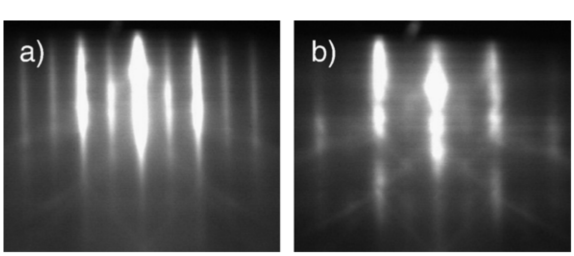

Fig. 1. RHEED patterns along the [100] direction of the initial $SrTiO_3$ substrate after annealing at a) 1023 K, b) 923 K.

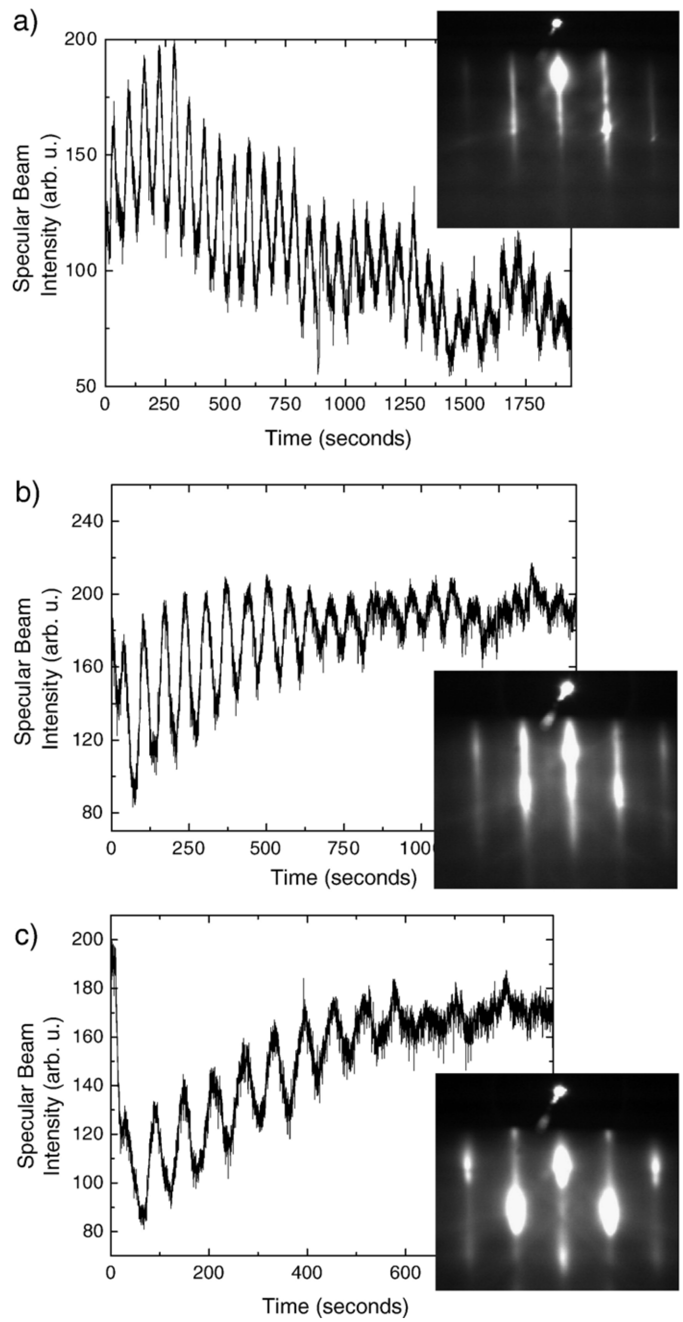

Fig. 2. RHEED oscillations of the specular spot intensity and final patterns for homo-epitaxial growth of $SrTiO_3$ thin films at various substrate temperature: a) 1023 K, b) 723 K, c) 523 K. The growth rate is in all cases of 2 MLs/min.

$SrTiO_3$ layer of ~3 MLs equivalent thickness was deposited on silicon at 523 K and the initial partial oxygen pressure of 5.3×10^{-6} Pa was slightly increased to 2.7×10^{-5} Pa to ensure good oxidation of titanium.

After annealing at 823 K under $P(O_2)=2.7\times10^{-5}$ Pa for ~10 min, crystallization of this $SrTiO_3$ buffer layer occurred. In a second step, Sr and Ti elements were co-evaporated under 2.7×10^{-5} Pa of molecular oxygen at different substrate temperatures.

Two ways of elaboration of the buffer layer have been compared: in the first, Sr and Ti were co-evaporated under O_2 to