Ferroelectric Oxide Single-Crystalline Layers by Wafer Bonding and Hydrogen/Helium Implantation

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ABSTRACT

Layer splitting by helium and/or hydrogen and wafer bonding was applied for the transfer of thin single-crystalline ferroelectric oxide layers onto different substrates. The optimum conditions for achieving blistering/splitting after post-implantation annealing were experimentally obtained for LiNbO$_3$, LaAlO$_3$, SrTiO$_3$ single crystals and transparent PLZT ceramic. Under certain implantation conditions large area exfoliation instead of blistering occurs after annealing of as-implanted oxides. Small area single-crystal oxide layer transfer was successfully achieved.

INTRODUCTION

One of the main demands for the integration of functional materials, including ferroelectric oxides, is the availability of high-quality oxide thin layers on technological important substrates. In recent years a major effort has been directed towards integration of oxide materials into semiconductor technology. Epitaxial growth approach lead to single-crystalline films, but for a large lattice mismatch in the percentage range a high density of threading dislocation can hardly be avoided if a critical thickness has been exceeded. Layer transfer by hydrogen implantation and wafer bonding is one of the promising approaches for non-lattice-matched materials integration allowing fabrication of complex heterostructures, which cannot be obtained by classical thin film deposition methods [1]. This technology, also known as “Smart-Cut®, “layer splitting”, or “layer exfoliation”, was first introduced by Bruel [2] in 1995 as a highly effective method for the fabrication of high quality silicon-on-insulator (SOI) wafers. Briefly a donor wafer is implanted with helium and/or hydrogen at a certain energy with doses ranging from $10^{16}$ up to $10^{17}$ cm$^{-2}$. The as-implanted donor wafer is then bonded to a host wafer and annealed at elevated temperatures, first to increase the bonding energy, and then to achieve splitting.

Application of the layer splitting approach for complex oxides is an attractive alternative to fabricate thin single-crystalline oxide films with precise thickness on any substrate at low temperatures [3]. It was previously shown that in order to achieve splitting after a post implantation annealing the wafer temperature during implantation must fall within a window that is specific to each material [4]. For perovskite oxides the temperature window is rather narrow making the layer transfer a relatively difficult process.

The present paper shows our latest achievements concerning layer splitting of oxide materials including the optimization of the implantation parameters as well as the annealing conditions for layer splitting. It shows also for the first time the transfer of small area single-crystal oxide layers with sub-micron thicknesses.
EXPERIMENTAL

In the present study 10 mm × 10 mm × 1mm substrates of single-crystalline SrTiO$_3$ (STO), LiNbO$_3$ (LNO), LaAlO$_3$ (LAO) and transparent poly-crystalline PLZT ceramic materials were used. In order to avoid the beam heating effect during implantation all samples were mounted onto silicon wafers using silver paste. Hydrogen (H$_2^+$) and/or helium (He$^+$) implantation was performed in a standard implanter at different temperatures ranging from room-temperature (RT) up to 300°C. To minimize ion channeling implantation was performed under 7° sample tilt. The influence of a two-step He + H co-implantation on blistering/splitting of oxide materials was also investigated: a low He dose (5.0 × 10$^{15}$ cm$^{-2}$) was first implanted at 105 keV followed by range matched H$_2^+$ (2.0 ÷ 5.0 × 10$^{16}$ cm$^{-2}$) implantation.

The as-implanted samples were annealed in air at a temperature ranging from 250°C up to 700°C in order to determine the temperature of the on-set of blistering. Nomarski optical microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate blister formation and exfoliation. Formation of platelet-like defects and their evolution after annealing were analyzed by cross section transmission electron microscopy (XTEM) at 200 kV.

RESULTS AND DISCUSSIONS

Blistering and exfoliation

During implantation a high density of extended defects such as platelets, bubbles and micro-cracks are formed. These defects are nucleation centers for the agglomeration of diffusing He or H during annealing. The growth of micro-cracks filled with He and/or H is responsible for splitting. For as-implanted samples that are not stiffened by being bonded to another substrate surface blistering occurs during annealing. Blistering is closely related to the formation of He/H-induced micro-cracks, which are also required to obtain layer splitting for bonded wafers.

In order to obtain the optimum implantation conditions all as-implanted samples were annealed and then investigated for blistering. The implantation temperature was validated if the blistering occurs at annealing temperature falling in the temperature range of 250 – 700°C. For a given implantation energy and dose the range of optimum implantation temperatures obtained are completed in Table I. The optimum implantation of STO and LNO is at room temperature, while PLZT and LAO need to reach a temperature of about 200°C during the implantation process.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dose (cm$^{-2}$)</th>
<th>Energy (keV)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO</td>
<td>5.0 × 10$^{16}$ H$_2^+$</td>
<td>130 - 160</td>
<td>RT</td>
</tr>
<tr>
<td>STO</td>
<td>5.0 × 10$^{15}$ He$^+$</td>
<td>105</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>2.0 ÷ 5.0 × 10$^{16}$ H$_2^+$</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>LNO</td>
<td>5.0 × 10$^{16}$ He$^+$</td>
<td>105</td>
<td>RT</td>
</tr>
<tr>
<td>LAO</td>
<td>5.0 × 10$^{16}$ H$_2^+$</td>
<td>130</td>
<td>200 ÷ 300</td>
</tr>
<tr>
<td>PLZT</td>
<td>5.0 × 10$^{16}$ He$^+$</td>
<td>105</td>
<td>200</td>
</tr>
</tbody>
</table>
During the blistering experiments it was unexpectedly observed that certain implantation conditions lead to large area exfoliation instead of blistering after annealing of as-implanted samples. This was the case for H-implanted STO, He-implanted LNO as well as for He+H co-implanted STO (figure 1a and 1b), while after annealing of H-implanted LAO and He-implanted PLZT broken blisters are observed (figure 1c and 1d).

Figure 1. SEM images of a) He+H co-implanted STO, b) He-implanted LNO, c) H-implanted LAO and d) He-implanted PLZT after 500°C annealing.

Large area exfoliation is directly related to a small size and/or a narrow distribution of the platelets and their evolution with annealing. XTEM (figure 2a) investigation shows that a high density of H-platelets of about 10 nm lateral size are formed during H-implantation into STO. Additionally, in the as-implanted LAO H-platelets have larger lateral sizes and distribution over the whole damaged region, as shown in figure 2b.
Figure 2. Cross section TEM images showing H-platelets in as-implanted STO implanted at RT with $5.0 \times 10^{16}$ H$_2^+$/cm$^2$ at an energy of 130 keV (a) and LAO implanted at 300°C with $5.0 \times 10^{16}$ H$_2^+$/cm$^2$ at an energy of 130 keV (b).

The as-implanted samples were annealed at elevated temperatures and the on-set of blistering/exfoliation was obtained for each investigated oxide. The activation energies ($E_a$) of blistering and exfoliation was estimated from the Arrhenius relationship: $1/t_b \sim \exp (-E_a/kT)$, where $t_b$ is the blistering time, which is the time of the on-set of blistering, $k$ is the Boltzmann constant and $T(K)$ the absolute temperature (see figure 3).

Figure 3. Activation energies of blistering/exfoliation of a) H$_2^+$ ($5.0 \times 10^{16}$ cm$^{-2}$, 130 keV) - implanted LAO at 200°C, b) H$_2^+$ ($5.0 \times 10^{16}$ cm$^{-2}$, 130 keV) - implanted STO at RT, c) He + H co-implanted STO (He$^+$: $5.0 \times 10^{15}$ cm$^{-2}$, 105 keV; H$_2^+$: $5.0 \times 10^{16}$ cm$^{-2}$, 130 keV) at RT and d) He$^+$ ($5.0 \times 10^{16}$ cm$^{-2}$, 105 keV) - implanted PLZT at 200°C.
Layer splitting

Oxide single crystals implanted by helium and/or hydrogen under conditions which allow blistering/exfoliation were used for layer splitting. The first attempt to direct bonding of the H-implanted STO to a host STO substrate failed due to a relatively high micro-roughness (>1nm) of the STO surfaces. Therefore, different bonding procedures via various intermediate layers such as spin-on glass (SOG), Au, etc. were used in order to transfer a single-crystalline layer onto different substrates. Successful layer transfer of single-crystalline STO has been achieved by annealing of the bonded pairs at temperatures under 300°C. Nevertheless, due to non-homogeneity of the bonding interface, the transferred layers shattered into pieces of about several hundred micron across (see Fig. 4). In the LAO case, due to a high micro-roughness of about 3 nm given by the existence of twin structures in the crystal, bonding of LAO on different substrates by direct wafer bonding could not be obtained. Further improvement of the surface conditions of single crystalline LAO substrates through fine polishing or surface activation will solve the bonding problem, as shown previously [5].

![Figure 4. (a) plan-view and (b) cross-section SEM images of a STO transferred layer](image)

CONCLUSIONS

A layer splitting approach combining helium and/or hydrogen implantation and wafer bonding was applied for the transfer of thin oxide layers onto different substrates. Blistering and exfoliation of oxides was shown. The specific implantation conditions for achieving blistering/splitting after a post-implantation annealing were successfully determined for each investigated oxide. Under certain implantation conditions large area exfoliation instead of blistering occurs after annealing of as-implanted oxides. Small area single-crystal oxide layer transfer was successfully achieved.
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