

# Ferroelectric-semiconductor heterostructures obtained by direct wafer bonding

Marin Alexe,<sup>a)</sup> Gerhard Kästner, Dietrich Hesse, and Ulrich Gösele  
*Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany*

(Received 19 March 1997; accepted for publication 21 April 1997)

A novel fabrication process of ferroelectric-semiconductor heterostructures based on direct wafer bonding has been demonstrated. Polycrystalline  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ferroelectric thin films were deposited on 3 in. silicon wafers using chemical solution deposition. The films were polished and then directly bonded to silicon wafers in a micro-cleanroom. After thermal annealing in air at 500 °C for 12 h, the bonding energy increases up to 1.5 J/m<sup>2</sup>. High resolution transmission electron microscopy shows the difference between the bonded and reacted interfaces. Obtaining a metal-ferroelectric-silicon (MFS) structure containing the ferroelectric-Si bonded interface was achieved by polishing down and etching the handling wafer. The  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  film kept its ferroelectric properties as shown by  $C-V$  measurement. © 1997 American Institute of Physics. [S0003-6951(97)02525-4]

In recent years a major effort has taken place to accomplish integration of ferroelectric materials into semiconductor technology. Ferroelectric capacitors have already been integrated into silicon integrated circuits to produce commercial nonvolatile memories.<sup>1,2</sup> Due to its simplicity and non-destructive readout, the idea of ferroelectric field effect transistor<sup>3</sup> as a memory cell remains a goal for ferroelectric-Si integration although realization attempts were so far not successful. Besides the memory effect, the photoelectric and pyroelectric effects in ferroelectric-semiconductor heterostructure<sup>4,5</sup> could be promising for developing new types of integrated detectors.

The success of integration basically is determined by the quality of the ferroelectric film and the process integration of the ferroelectric oxides into the semiconductor technology. The use of volatile, toxic, or undesirable elements as Pb and Bi in semiconductor technology remains one of the technological and environmental problems. Moreover, high temperatures that basically are required to obtain ferroelectric thin films with very good properties have to be avoided since high processing temperatures would lead to undesirable interface reaction at the semiconductor-ferroelectric interface. One way to avoid reactions is to grow a buffer layer between Si and the ferroelectric film.<sup>6</sup> The present work proposes a new approach for fabricating ferroelectric-semiconductor devices by direct bonding of ferroelectric thin films to a silicon wafer.

In the last decade, direct wafer bonding (DWB)<sup>7,8</sup> has drawn attention as a versatile method of fabricating silicon on silicon<sup>9</sup> or silicon on insulator (SOI) devices<sup>10,11</sup> as well as other materials combinations.<sup>12</sup> There are some reports on direct bonding of silicon wafers on bulk ferroelectrics.<sup>13,14</sup> The most difficult point on bonding bulk ferroelectric oxides to Si is the large mismatch between thermal expansion coefficients of the two materials<sup>13</sup> which limits the annealing temperature of the bonded pair, and consequently the achievable bonding energy. In this respect, too, the use of ferroelectric thin films instead of bulk ferroelectrics offers a principal advantage.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) thin films were obtained by chemical

solution deposition (CSD) method as described elsewhere.<sup>15</sup> BiT thin films were deposited onto *p*-type 3 in. Si wafers (1–10 Ω cm resistivity) by spin coating at 2000 rpm for 35 s. The metalorganic films were dried at 120 °C for 1 min and subsequently pyrolyzed on a hot plate at 300 °C for 5 min. To increase the film thickness, the whole procedure was repeated three times. The amorphous films were etched at the rim of the wafer in order to eliminate the inherent thickness nonuniformity from the spinning process. The etching was done using a standard photolithography process and chemical etching in buffered hydrofluoric acid. Finally, the BiT thin films were crystallized by conventional thermal annealing in air for 30 min at 575 °C. The film thickness measured by SEM was 580 nm.

The film surface morphology was analyzed using atomic force microscopy (AFM) (Digital Instruments, D5000). The film is polycrystalline with a grain diameter of about 100 nm. The roughness of the film computed from the AFM image is about 5 nm with a waviness of about 45 nm across a 10 × 10 μm<sup>2</sup> area.

As the bondability of a wafer depends on the roughness<sup>16</sup> and waviness<sup>8</sup> of the surface, the crystallized films were polished for 45 min using a standard tribochemical method with a polishing solution of pH 8.5 composed of Syton, H<sub>2</sub>O and glycerol (4:4:1). After polishing, the wafers were ultrasonically cleaned for 1 h in deionized water to remove any residue. AFM images of the polished films show a significant decrease of the roughness, and improved rms value of about 1.5 nm. The final film thickness was 400 nm.

The BiT/Si wafer which showed a hydrophilic surface was then bonded to a silicon wafer, covered with a native oxide, by a standard direct wafer bonding process in a micro-cleanroom setup.<sup>17</sup> Figure 1 shows an infrared photograph of a bonded wafer pair where the bonded area appears bright and dark contrast indicates incomplete bonding. It can be seen that in the upper part of the wafers a bubble and an incomplete bonded area are formed. This effect is due to a macroscopic defect, a radial thickness nonhomogeneity (street) in the BiT film caused by a dust particle during the spinning process.

The surface energy which characterizes the strength of the bonding was measured using the crack opening

<sup>a)</sup>Electronic mail: malexe@mpi-halle.mpg.de

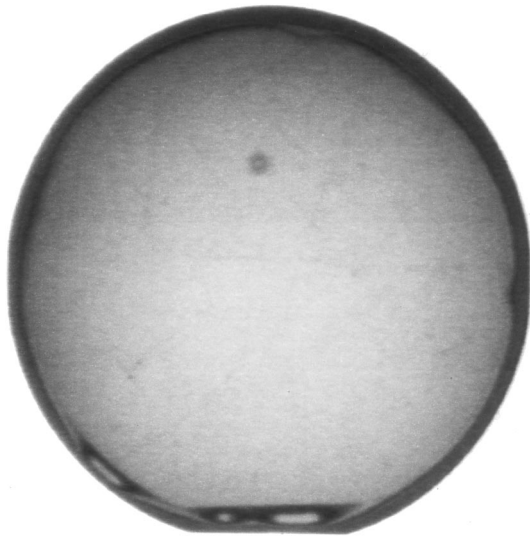
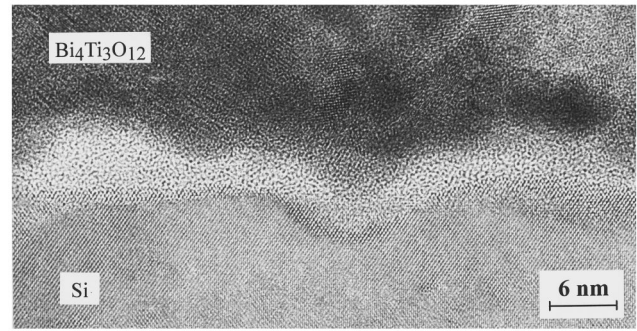


FIG. 1. Infrared transmission photograph of a 3 in.  $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Si}$  wafer bonded to a Si wafer.

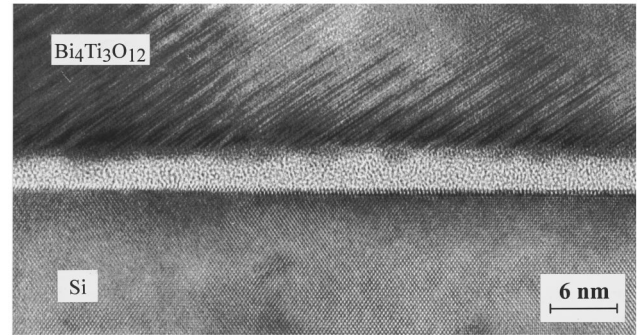
method.<sup>18</sup> The surface energy shows a drastic increase from as low as  $20 \text{ mJ/m}^2$  after room-temperature bonding to about  $1.5 \text{ J/m}^2$  after thermal annealing around  $500^\circ\text{C}$  for 12 h. The surface energy of the room-temperature bonded wafer is very low for a hydrophilic bonding. The reason for this low surface energy could be associated with the polycrystalline nature of the film. Due to the intergranular regions which act like microscopic voids, the actual bonded area is smaller than the entire surface.

Due to the high bonding energy, cross sections could be prepared by wire sawing and polishing. High resolution transmission electron microscopy (HRTEM) of these cross sections is shown in Fig. 2 where Fig. 2(a), represents the ‘‘reacted’’ BiT–Si interface formed by the film deposition on the handling wafer and crystallization annealing at  $575^\circ\text{C}$  for 1 h, while Fig. 2(b) shows the bonded BiT–Si interface after a thermal annealing at  $500^\circ\text{C}$  for 12 h. From the two pictures it can be seen that the Si and  $\text{SiO}_2$  of the handling wafer are affected by growing and annealing of the BiT film. In contrast, the silicon at the bonded interface remains unaffected even after annealing at  $500^\circ\text{C}$  for 12 h. It can be seen that after bonding the native silicon oxide is acting like a very thin buffer layer for the ferroelectric thin film.

For obtaining a metal-ferroelectric-silicon (MFS) structure with a ferroelectric-Si bonded interface, the handling wafer with the reacted interface was polished down to  $50 \mu\text{m}$ , and subsequently etched away in KOH at  $80^\circ\text{C}$ . Circular dots with a  $0.3 \text{ mm}$  diameter area were formed by Al film evaporation on top of the BiT film through a metallic mask. The bottom electrode of the structure was an evaporated Al film. Prior to Al deposition for the bottom electrode, the native silicon oxide was etched away in buffered hydrofluoric acid. The capacitance–voltage curve for the MFS structure with the bonded interface was measured at  $10 \text{ kHz}$  using a Hewlett-Packard HP4192 impedance analyzer. The  $C$ – $V$  measurements presented in Fig. 3 reveal a clockwise hysteresis which is due to a real ferroelectric switching and confirms that the BiT film is still ferroelectric.<sup>19</sup> Further measurements are now in progress in order to characterize the



(a)



(b)

FIG. 2. High resolution TEM pictures of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ –Si for (a) the reacted interface, and (b) the bonded interface, after heating for 12 h at  $500^\circ\text{C}$ .

BiT–Si bonded interface and MFS structure with transferred BiT films.

In summary, direct bonding of large area  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  thin films on silicon was demonstrated. Annealing of the room-temperature bonded wafers at  $500^\circ\text{C}$  for 12 h drastically increased the bonding energy without leading to undesirable interface reactions. Transferring of a ferroelectric thin film on a silicon wafer employing direct bonding coupled with thinning down the handling wafer and the fabrication of a

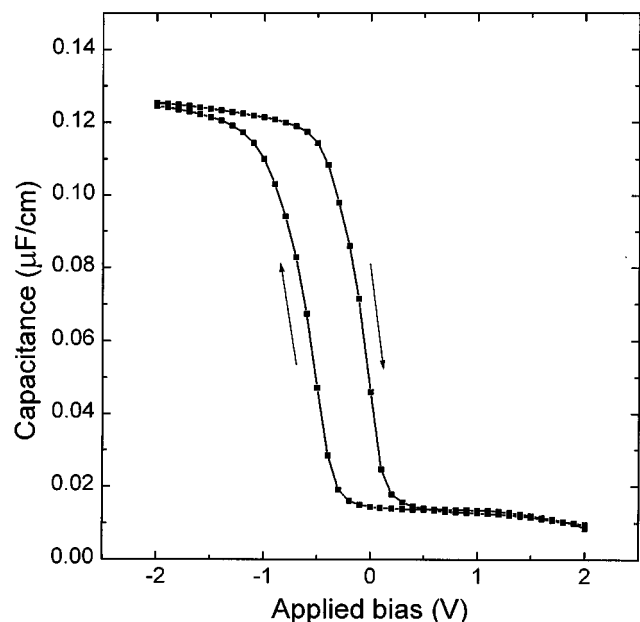


FIG. 3. Capacitance–voltage curve for a MFS structure with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ –Si bonded interface measured at  $10 \text{ kHz}$ .

MFS structure with a well-defined bonded interface were demonstrated. In this context, it should be mentioned that for practical fabrication structures the thinning of the Si handling wafer could be replaced by a hydrogen implantation prior to wafer bonding and a subsequent splitting (“smart cut”) of the silicon wafer during heating after bonding.<sup>20</sup> *C–V* curves of the MFS structures show a hysteresis which is due to the ferroelectric properties of the transferred  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  film. It remains to be seen whether in contrast to the directly deposited and annealed ferroelectric films on silicon, the ferroelectric film bonded to silicon keep desirable retention properties as required for fabricating ferroelectric field effect transistors.

The authors would like to thank R. Scholz for taking the high resolution TEM micrographs.

<sup>1</sup>J. F. Scott and C. A. Paz de Araujo, *Science* **246**, 1400 (1989).

<sup>2</sup>T. Sumi, N. Moriwaki, G. Nakane, T. Nakakuma, Y. Judai, Y. Uemoto, Y. Nagano, S. Hayashi, M. Azuma, T. Otsuki, G. Kano, J. D. Cuchiaro, M. C. Scott, L. D. McMillan, and C. A. Paz de Araujo, *Integr. Ferroelectr.* **6**, 1 (1995).

<sup>3</sup>S. Y. Wu, *IEEE Trans. Electron Devices* **ED-21**, 499 (1974).

<sup>4</sup>Y. Xu, C. J. Chen, R. Xu, and J. D. Mackenzie, *Phys. Rev. B* **44**, 35 (1991).

<sup>5</sup>L. Pintilie, M. Alexe, I. Pintilie, and T. Botila, *Appl. Phys. Lett.* **69**, 1571 (1996).

<sup>6</sup>J. Yu, Z. Hong, G. Cao, J. Xie, X. Li, S. Li, and Z. Li, *Appl. Phys. Lett.* **70**, 490 (1997).

<sup>7</sup>W. P. Maszara, *J. Electrochem. Soc.* **138**, 341 (1991).

<sup>8</sup>U. Gösele, H. Stenzel, M. Reiche, T. Martini, H. Steinkirchner, and Q.-Y. Tong, *Solid State Phenom.* **47–48**, 33 (1996).

<sup>9</sup>M. Shimbo, K. Furukawa, K. Fukuda, and T. Tanzawa, *J. Appl. Phys.* **60**, 2987 (1986).

<sup>10</sup>J. B. Lasky, *Appl. Phys. Lett.* **48**, 78 (1986).

<sup>11</sup>H. Baumgart, T. J. Letavic, and R. Egloff, *Philips J. Res.* **49**, 91 (1995).

<sup>12</sup>Z. L. Liau and E. Mull, *Appl. Phys. Lett.* **56**, 737 (1990).

<sup>13</sup>J. Haisma, B. A. C. M. Spierings, U. K. P. Biermann, and A. A. van Gorkum, *Appl. Opt.* **33**, 1154 (1994).

<sup>14</sup>A. Namba, M. Sugimo, T. Ogura, Y. Tomita, and K. Eda, *Appl. Phys. Lett.* **67**, 3275 (1995).

<sup>15</sup>M. Alexe, A. Pignolet, S. Senz, and D. Hesse, *Ferroelectrics* (to be published).

<sup>16</sup>B. E. Roberts and S. N. Farrens, *J. Electrochem. Soc.* **143**, 2365 (1996).

<sup>17</sup>T. Stengl, K.-Y. Ahn, and U. Gösele, *Jpn. J. Appl. Phys. 1* **27**, 236 (1988).

<sup>18</sup>W. P. Maszara, G. Goetz, A. Caviglia, and J. B. McKitterick, *J. Appl. Phys.* **64**, 4943 (1988).

<sup>19</sup>J. F. Scott, in *Ferroelectrics Ceramics*, edited by N. Setter and E. L. Colla (Birkhauser, Basel, 1993), p. 194.

<sup>20</sup>M. Bruel, *Electron. Lett.* **31**, 1201 (1995).