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Electrical Characterization of the Interface in Unitype Silicon Structures Obtained by Means of Solid-State Bonding

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Abstract

The properties of the interface in isotype structures formed by solid-state bonding (SSB) of silicon wafers with the same type of conductivity are investigated depending on the technology of bonding. In order to reveal the role of oxygen in the electric properties of the interface, bonding was carried out both using the wafers coated with the natural oxide (not thicker than 1–2 nm) and using specially oxidized ones (with silicon oxide layer up to 20 nm). The investigation of bicrystals bonded after bringing together in air or deionized water, demonstrated that in this case the electric activity of the interface is determined mainly by the degree of its enrichment with oxygen and contamination of the surfaces of wafers to be bonded with acceptor impurities (presumably aluminium). Electric activity of oxygen-free interface in the structures obtained by combining wafers ion etching and annealing in vacuum depends mainly on mismatching of the lattices of wafers to be spliced. The properties of SSB structures with the buried oxide layer obtained by bonding of the silicon wafers of n-type conductivity are determined by the contamination of the bonding interface with an acceptor impurity.

INTRODUCTION

The properties of devices and structures, obtained on the basis of the solid-state bonding technology (SSB) using silicon plates, should be substantially dependent on the state of the interface “silicon – silicon” in the case of the devices of power electronics, and “silicon – silicon oxide” in the structures “silicon on insulator” (SOI) [1–3].

In the general case, from the viewpoint of crystallographic structure, the silicon–silicon interface in isotypic SSB bicrystals is identical with the boundary of the twist-type grains [4] and may be described within the frame of the standard model of the double Schottky barrier for grain boundaries (GB) in polysilicon [5]. According to [6–8], electric activity of GB in polysilicon is determined by the dangling bonds due to mismatching of the lattices of the neighbouring grains (intrinsic), and by the formation of a specific impurity-defect atmosphere in the neighbourhood of the interface (extrinsic activity). In this sense, the electric activity is usually exhibited as a barrier capacitance and non-linearity of voltage-current I–V characteristics under electric field applied across the boundary plane [5, 8].

It should be noted that the interface formed during bonding of silicon wafers is usually characterized by substantially higher oxygen content in its neighbourhood (because of the direct contact with the oxygen of air before the wafers are put together) than for GB in polysilicon. Because of this, from the viewpoint of the above considerations, electric activity of the interface in SSB silicon bicrystals should be considered rather induced than intrinsic. This is even more true for the investigation of the interface in SOI structures because in this case two silicon wafers are not in direct contact but are separated by an intermediate (buried) oxide layer. In this sense, the “silicon – silicon oxide” boundary cannot be considered as a simple twist-type boundary. So, the activity of the interface in such a “bicrystal” will be determined not only by mismatching of the SiO_2 lattice and the lattice of silicon after bonding but also by the defects in silicon oxide itself [9].

So, all the above-mentioned considerations allow us to conclude that when interpreting electric properties of the interface in SSB one should take into account the substantial role of oxygen.

To investigate the properties of the interface as it is (without additional effect of the p–n junction), we studied the so-called isotype bicrystalline structures formed by direct bonding of the silicon wafers of one type of conductivity (p–p or n–n). In order to reveal the role of oxygen in the electric properties of the interface, the wafers covered with native oxide (not thicker than 1–2 nm) were bonded, as well as those specially coated with a layer of thermal oxide (up to 20 nm thick). Besides, we investigated the effect of the environment in which the wafers were brought together before bonding, the environment in which the annealing was carried out during bonding, and the crystrallographic misorientation of the crystals to be bonded, on the electric properties of the interface.

EXPERIMENTAL

In order to obtain bicrystalline SSB structures, we used commercially available polished wafers of the n- and p-type with (100) orientation and resistivity of 1 – 20 Ω cm. The characteristics of the initial wafers, the regimes of chemical and other kinds of treatment of the wafers before bonding, as well as the regimes and conditions of bonding are listed in Table 1. We investigated 4 groups of the SSB structures: (***a***) wafers were rinsed in deionized water, dried, joined and annealed in air at 1150 °C; (***b***) wafers were joined in deionized water, dried and annealed in air at 1150 °C; (***c***) after ion etching, the wafers were brought into face-to-face contact and annealed in vacuum at 1200 °C under the pressure of $3 \cdot 10^6$ Pa; (***d***) one of the wafers was subjected to thermal oxidation, then the wafers were joined and annealed in air at 1150 °C. It should be noted that some wafers belonging to the groups ***a***, ***b*** and ***c*** were specially misoriented when contacting thus forming the twist-type boundaries.

For the electric characterization of the bicrystalline samples, the transversal static voltage-current (I–V) characteristics and high-frequency capacitance voltage characteristics (C–V) were measured within the temperature range 77–300 K.

DISCUSSION

Group a. Experiments showed that the interface in p-type bicrystals (series 3–5) of this group does not exhibit electric activity possessing linear I–V and inductive character of impedance. However, in n–n bicrystals with hydrophilic surface (series 1) I–V becomes symmetrically-nonlinear within the whole temperature range, the transversal resistance of the bicrystal increases sharply, while the impedance becomes of the capacitance character (Fig. 1). The latter is usually attributed to the formation of p–n junction due to the contamination of the interface with aluminium when the wafers are treated in peroxide-ammonium solution [10, 11]. An evidence in favour of this assumption is the linearity of C–V of the structures in the coordinates $C^{-3}(V)$, which is known

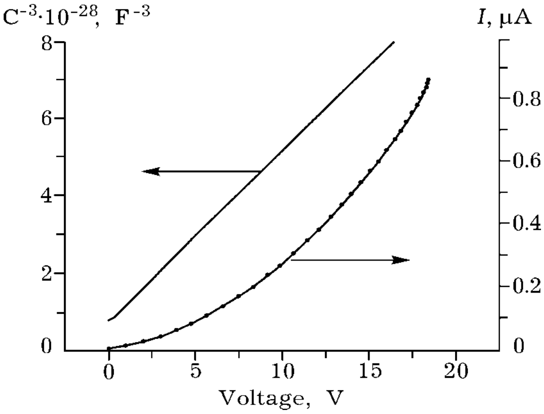

Fig. 1. I–V and C–V characteristics of the n–n bicrystal of the series 1 from the group ***a*** at room temperature.

TABLE 1

Characteristics of wafers and bonding technology

Group	Series	Characteristics of bonded wafers	Joining environment	Modes of chemical treatment and bonding
a	1	*n*-type, $\rho = 4.5\ \Omega$ cm, (100), oxide layer thickness ~2 nm, misorientation angle $\theta = 0°$	Air	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
	2	*n*-type, $\rho = 4.5,\ \Omega$ cm, (100), oxide layer thickness ~1 nm, $\theta = 0°$	»	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) HF solution to remove oxide 4) Rinsing in deionized water 5) Annealing in air at 1150 °C, 1 h
	3	*p*-type, $\rho = 2\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 0°$	»	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
	4	*p*-type, $\rho = 20\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 0°$	»	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
	5	*p*-type, $\rho = 2\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 20°$	»	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
b	1	*p*-type, $\rho = 1\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 20°$, perifery of sample	Deionized water	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
	2	*p*-type, $\rho = 1\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 20°$, center of sample	» »	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
	3	*p*-type, $\rho = 1\ \Omega$ cm, (100), oxide layer thickness ~2 nm, $\theta = 20°$, medium part of sample	» »	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Annealing in air at 1150 °C, 1 h
c	1	*p*-type, $\rho = 12\ \Omega$ cm, (100), oxide layer thickness < 1 nm, $\Sigma 3$, $\Delta\theta = 3$	Vacuum	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Ion etching 4) Annealing in vacuum 10^{-7} Pa at 1200 °C under the pressure of $3 \cdot 10^6$ Pa, 10 h
	2	*p*-type, $\rho = 2\ \Omega$ cm, (100), oxide layer thickness < 1 nm, $\theta = 20°$	»	1) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 2) Rinsing in deionized water 3) Ion etching 4) Annealing in vacuum 10^{-7} Pa at 1200 °C under the pressure of $3 \cdot 10^6$ Pa, 10 h
d	1	*p*-type, $\rho = 2\ \Omega$ cm, (100), oxide layer thickness ~20 nm, $\theta = 0°$	Air	1) Oxidation of one of the wafers at 900 °C, 15 min 2) $NH_4OH:H_2O_2:H_2O = 1:8:1$ 3) Rinsing in deionized water 4) Annealing in air at 1150 °C, 1 h
	2	*n*-type, $\rho = 4.5\ \Omega$ cm, (100), oxide layer thickness ~20 nm, $\theta = 0°$	»	1) Oxidation of one of the wafers at 900°C, 15 min 2) $NH_4OH:H_2O_2:H_2O=1:8:1$ 3) Rinsing in deionized water 4) Annealing in air at 1150 °C, 1 h

to take place for a smooth p–n junction (see Fig. 1). Besides, after the surface layer of wafers contaminated with acceptors is removed by the solution of hydrofluoric acid directly before bonding (series 2), the properties of n–n bicrystals turn out to be similar to those in p–p bicrystals. It should be noted that in case of a 20° misorientation of the wafers to be bonded (series 5) the properties of bicrystals of the group ***a*** do not change.

Group b. Bicrystals of this group possessed increased oxygen content in the vicinity of the interface because the p-type wafers were brought together before bonding in deionized water. Oxygen concentration turned out to be the largest at the periphery and the smallest in the center of bicrystal. Experiments showed that in this case the electric properties of the interface depended on the place from which the samples are cut off the SSB structure. The samples from the central part (series 2) had Ohm-type I–V (curve *2* in Fig. 2) and transversal resistance close to that for the wafers to be bonded. For the samples cut off the peripheral regions of the group ***b*** bicrystals (series 1) the transversal resistance was much higher; I–V were nonlinear and exhibited a strong hysteresis (curve *1* in Fig. 2). At the same time, the samples of the series 3 cut off the regions between the center and periphery of the bicrystal were characterized by nonlinear I–V but without any hysteresis (curve *3* in Fig. 2). It should be noted that for the samples of the series 1 long-time relaxations of conductance and capacitance were typical (characteristic time being up to thousands seconds at decreased temperature) after stepwise changes of the applied voltage (Fig. 3). As it is demonstrated in [7, 9, 12], the mentioned relaxation is due to the presence of special trapping centers located inside the islands of SiO_x phase formed in the vicinity of the interface which are able to get re-charged when bias voltage is applied. When the voltage is switched off (on), the traps are emptied (filled) slowly due to the tunneling of the trapped charge carriers through oxide layer. The kinetics of this process in SSB bicrystals and silicon polycrystals was studied in detail in [7, 9, 12].

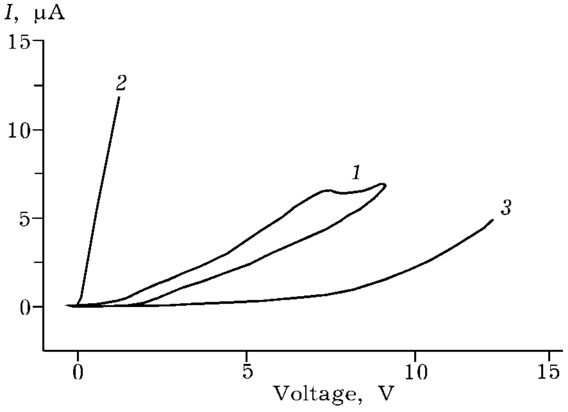

Fig. 2. Voltage-current characteristics of the samples cut of the peripheral (*1*), central (*2*) and intermediate (*3*) regions of the p–p bicrystal of the group ***b***.

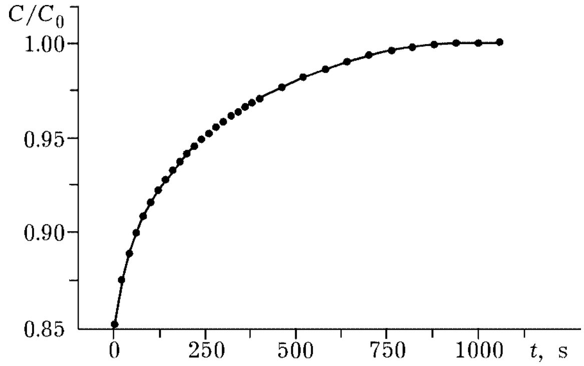

Fig. 3. Relaxation of the capacitance of the interface of a sample cut off the peripheral part (series 1) of the p–p bicrystal of the group ***b*** after the transversal shift voltage is switched off (normalized for the equilibrium capacitance C_0) at 220 K.

For the example of the samples of this group, one can see that there is a direct correlation between the oxygen content at the boundary and electric properties exhibited by this boundary.

Group c. Experiments showed that in the case of bicrystals with practically oxygen-free interface, electric activity depends on the misorientation angle between wafers to be bonded. For example, both weakly deviated from the special orientation Σ3 (series 1) and those with strongly deviated twist boundary (series 2) are characterized by linear I–V. However, in the latter case the resistance of the boundary exceeds the resistance of the wafers to be bonded by more than order of magnitude. It is natural to refer the latter fact to the presence of dangling bonds arising as a result of mismatching of the lattices of wafers to be bonded [13].

Group d. Let us consider the properties of the interface in the structures of the type p–

SiO_2–p and n–SiO_2–n obtained by bringing together silicon wafers of the same conductivity type, one of them being oxidized preliminarily and another not pre-oxidized. The thickness of thermally grown oxide layer was about 20 nm. Investigations showed that the buried oxide layer provides a substantial increase of the transversal resistance of SSB structures in comparison with that for bicrystals obtained by bonding the wafers coverted with native oxide. The symmetry of I–V is observed for the p–SiO_2–p structures (series 1), as well as a smooth reversible breakdown of the oxide at voltage above $V = 5$ V (curve *1* in Fig. 4). The behaviour of C–V for all the samples of this group is similar to that for MOS structure in the mode when the channel is depleted by the carriers (curve *1* in Fig. 5). It follows from the fact that the density of charge states at both boundaries of the buried oxide with silicon is approximately similar and no slow re-charging takes place on them. At the same time, the equilibrium transversal conductivity after breakdown in these structures was found to be much higher than the known models of electric transfer in silicon oxide suggest [14]. These facts allow us to conclude that the properties of oxide after splicing are rather nonhomogeneous by the boundary plane, which allows one to connect a smooth transition of SSB structures into better conducting state at an increase of the bias voltage above 5 V with the reversible heat breakdown.

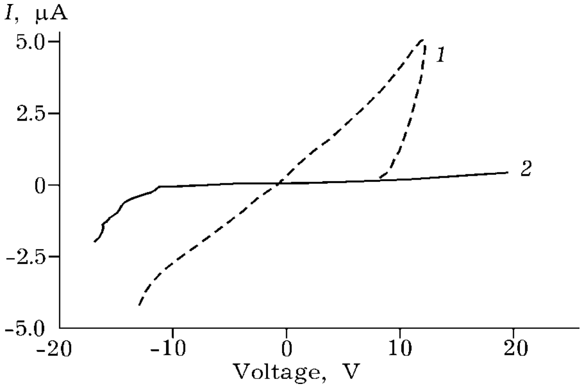

Fig. 4. I–V characteristics of the samples of group ***d*** with the buried oxide layer for p–p bicrystals (*1*) and n–n bicrystals (*2*).

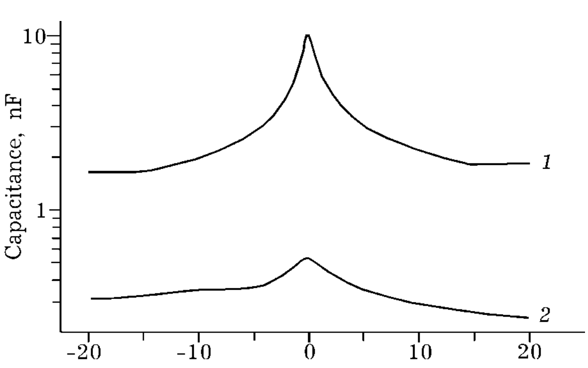

Fig. 5. C–V characteristics of the samples of the group ***d*** with the buried oxide layer for p–p bicrystals (*1*) and n–n bicrystals (*2*).

As one can see in Fig. 5, the cross I–V and C–V for n–SiO_2–n structures (series 2) are substantially asymmetrical. One of the reasons may be the difference in the properties of the interfaces "silicon – SiO_2" at both sides of the buried oxide layer due to different formation conditions: thermal oxidation in one case (oxidation interface) and bonding in the other case (interface of bonding). However, this contradicts to the results of investigation of the structures similar to p–SiO_2–p for which the symmetry of electric properties was observed. Because of this, the properties of the bicrystals of series 2 of this group can be explained by the contamination of the vicinity of interface of bonding with aluminium. Since oxide is located to one side of this interface, the diffusion of aluminium into the plates will lead to the formation of only one p–n junction, which will determine the asymmetry of properties exhibited by the structures of this type.

CONCLUSIONS

The investigation of unitype silicon bicrystalline structures obtained using SSB after bringing the wafers together in air or in deionized water allows us to state that the electric activity of the "silicon–silicon" interface in this case is extrinsic (not intrinsic) because it is determined mainly by the degree of its enrichment with oxygen and by the contamination of the surfaces of the bonded wafers with acceptor impurities (presumably aluminium). In the case of structures obtained by joining of ion-etched wafers and their annealing in vacuum, the electric activity of oxygen-free interface is practically absent. The properties of

SSB structures with the buried oxide layer obtained by bonding silicon wafers of n-type conductivity are determined by the contamination of the interface of bonding by acceptor impurity.

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