Ultra-Shallow p-type Doping of Silicon by Atomic Layer Deposition of Al2O3 thin films on SiO_2/Si

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Sheet resistance at 925 ^{o}C

The two-stage behavior of SR vs. number of cycles is also observed for the samples annealed at 925 ^{o}C, presented in Fig. S1a. At the same time, for the samples annealed at 925 ^{o}C, the minimum SR is obtained for the sample deposited with Al_2O_3 of 70 cycles and annealed for 30 s (Fig. S1a).

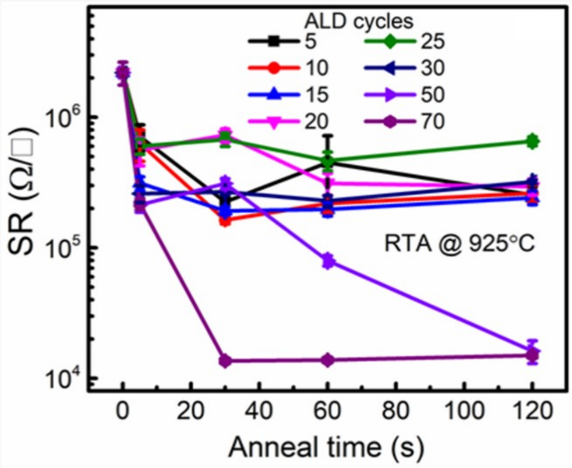

Fig. S1. *SR vs annealing time for different number of cycles of ALD annealed at 925 ^{o}C.*

Experimental procedures

Cleaning of Si wafer: Si substrates were diced to 1.5 X 1.5 cm and cleaned using acid piranha (3:1 H_2SO_4:30% H_2O_2) for 20 min in a sonication bath at 60 ^{o}C followed by base piranha solution (5:1:1 H_2O:27% NH_4OH:30% H_2O_2) in a sonication bath at 60 ^{o}C for 8 min.

Al_2O_3 deposition by ALD: Al_2O_3 layer was deposited by atomic layer deposition using Ultratech Savannah G2 ALD System. For the Al doping study, Al_2O_3 layers of different thicknesses were deposited at 150 ^{o}C using TMA and water as precursors at a growth rate of ~1Å/cycle.

Ellipsometry measurements: Layer thickness measurements were performed using J.A. Woolam Co. variable-angle VB-400 spectroscopic ellipsometry system (VASE). The thickness of the oxide layer at each stage of the experiment, i.e SiO_2 layer thickness after piranha cleaning, Al_2O_3 layer thickness after deposition and, and after RTA step were monitored step-wise using the ellipsometry measurements.

Rapid thermal annealing: RTA was carried out using AnnealSys AS-Microsystem. Prior to anneal process, the chamber was purged with argon and evacuated to 0.09 mbar. During the annealing process the samples were rapidly heated to a set temperature for specified time durations of 5-120 s.

Four-point sheet resistance measurements (SR): sheet resistance measurements were carried out using Jandel RM3-AR setup.

X-ray photoelectron spectroscopy (XPS): XPS data was recorded using X-Ray Photoelectron Spectroscope Axis Supra (Kratos). Spectra were acquired with monochromatic Al(Kα) radiation. XPS data fitting was performed using the XPSPEAK41 software using linear background correction.

Time-of-Flight Secondary-Ion-Mass-Spectroscopy (TOF-SIMS): TOF-SIMS measurements were performed using ION-TOF GmbH TOF.SIMS 5 system. The depth profiles were taken in a dual mode using 25 KeV Bi+ analysis ions and 2kV Cs+ sputtering ions (at 45° incident). The sputter rate was 0.75 nm/sec. The sputtered area for all measurements was $300 \times 300\ \mu m^2$ and the acquisition area was $50 \times 50\ \mu m^2$. Data averaged over 5 points to decrease the noise. The depths were measured with profilometer, with error of +/-2nm. Every measurement was repeated 7 times to improve statistics of data.

Hall measurements - Hall effect measurements were carried at 80 K-300 K using LakeShore 8400 Series setup. To achieve ohmic contact, the Al_2O_3 layer is selectively removed at the four corners of the substrates using ion milling. Al contacts (100 nm thick) were selectively deposited at the corners of the substrates by evaporation following thermal anneal at 450 ^{0}C for 60 s in forming gas atmosphere.

For Hall effect measurements, Van der Pauw four probe configuration resistivity measurements were performed at room temperature to verify the sheet resistance and resistivity on 50 cycles of Al_2O_3 deposited sample annealed at 1005 ^{0}C for 60 s. To evaluate the Al doping in Si, the doping was carried out in a highly resistive Si substrates with sheet resistance in the order of MΩ (1-10 MΩ). The sheet resistance of the sample measured using Van der Pauw technique agrees with the sheet resistance measured by four-point probe method reaching 12.2 and 8.6 KΩ/□, respectively. Room temperature Hall effect measurements were carried out in a Van der Pauw configuration, to extract carrier density and mobility values. The Hall voltage is given by equation 1:

$$V_H = \frac{R_H I B}{d} \quad (1)$$

Where RH=1/ρ_e is the Hall coefficient for the p-type semiconductors, B is the applied magnetic field, I is the current flow and d is the thickness of the film. Low temperature Hall effect measurements were performed in temperature range of 80k-300k. The activation energy of Al dopants in Si can be calculated by linear fitting according to equation 2.

$$n(T) = C * \exp(-EA/k_BT) \quad (2)$$

Where K_B is the Boltzman constant, EA = Ea- Ev is the activation energy (Ea is acceptor level and EV is valence band), C is a constant C= $\frac{\sqrt{N_V N_A}}{2}$, N_V is the effective density of states in the valence band and N_A is concentration of acceptors

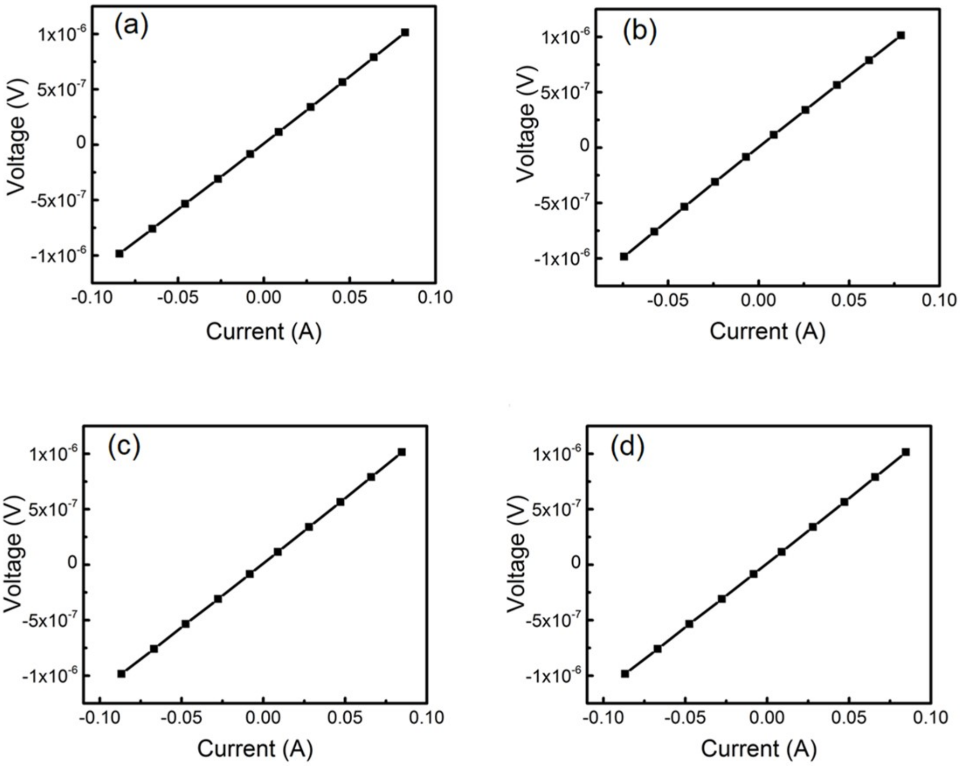

Fig. S2 *I-V curves from Van der Pauw measurements showing ohmic Al contacts (a) ohmic check for contact 1-2 (b) for contact 2-3 (c) for contact 3-4 (d) for contact 4-1*

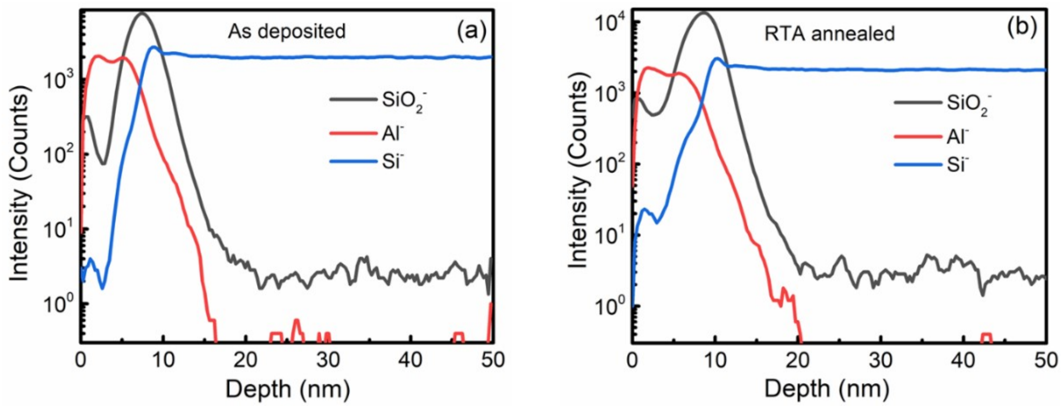

***Fig. S3**. TOF-SIMS analysis (a) as-deposited Al_2O_3 (b) following RTA.*

Thermal oxidation – Thermal oxidation of Si was performed using Expertech (Expert semiconductor technology Inc.

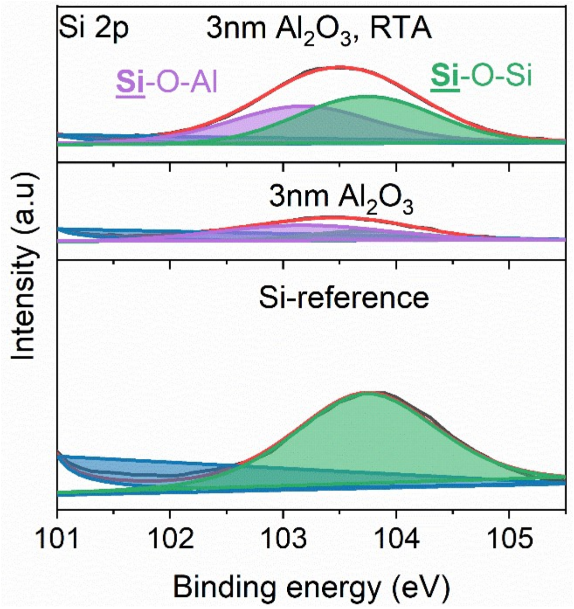

Fig. S4. Expanded view of 101-106 eV region Si 2p spectra. High-resolution XPS spectra for 3nm ALD Al2O3 deposited on Si substrate before and after RTA.

Capping test was done by encapsulating the Al_2O_3 with evaporated thermal SiO_2 where the total thickness of (Al_2O_3+SiO_2) was kept constant to 15 nm and the thicknesses of Al_2O_3 + SiO_2 are varied individually as 15+0, 11+4, 7+8, 5+ 10, 3+ 12 and 0+15 nm, respectively. RTA was performed at 1005 ^{0}C for 60 s for the SiO_2 capped samples. For comparison, samples were prepared without SiO_2 capping with same Al_2O_3 thicknesses (15, 11, 7, 5, and 3 nm) and annealed under the same conditions as that of the SiO_2 capped substrates.