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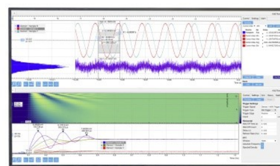

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A study of capping layers for sulfur monolayer doping on III-V junctions

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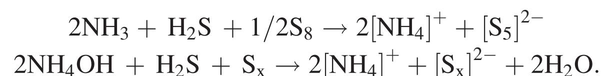
Recently, high dosage doping on Si multi-gate field effect transistors and III–V planar structures using a self-limiting monolayer doping technique was reported to overcome challenges in scaling nano-sized transistors. The stoichiometry or composition of the capping layer was found to affect the diffusion efficiency of this process. In this work, we study the effect of a capping layer in sulfur monolayer doping on III–V junctions. Various capping temperatures and growth methods were compared. Based on the theoretical and experimental results, we suggest an optimized scheme consisting of a bi-layer capping structure. From Hall measurements and secondary ion mass spectrometry, a SiN_x/BeO bi-layer capping, compared to single layer cap, exhibited the best results with a surface sheet resistance of 232 Ω/sq, junction depth of 11 nm, dopant profile abruptness of 3.5 nm/dec, electrically active S concentration of $4.9 \times 10^{19}/cm^3$ ($=1.34 \times 10^{13}/cm^2$), and 3 times higher activation efficiency without significant transient-enhanced dopant diffusion. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4772641]

Three dimensional structures such as multi-gate field effect transistors (FinFETs) with III–V materials such as GaAs, InGaAs, and InAs for the NMOS channel are increasingly popular because their superior electron mobilities promise to enable density and gate length scaling in future technology nodes. As gate length scaling progresses, the conventional doping technique using ion implantation is challenged by random dopant fluctuations and a non-uniform vertical doping profile around a high aspect ratio fin structure.[1,2] Recently, a controllable, nanoscale doping technique for Si and III–V substrates using molecular monolayers was able to achieve sub-5 nm ultra-shallow junctions.[3] Research has demonstrated that a monolayer doping (MLD) technique provides damage-free and high dose control of the dopants. The self-limiting nature of the monolayer formation reaction also results in higher uniformity than conventional surface doping techniques such as ion and plasma implantation.[4,5]

A chemical vapor deposition (CVD)- or atomic layer deposition (ALD)-based capping layer for MLD is preferable to a physical vapor deposition scheme due to the need for conformity in 3D structures such as III–V FinFETs. However, because of the low thermal stability of sulfur ions, the number of sulfur elements (or dose) at the channel surface is strongly dependent on the growth temperature and precursor chemistry of the capping material. It also has been reported that the stoichiometry and composition of the capping layer can affect the diffusion efficiency of this MLD process.[1] Here, to more precisely understand sulfur (S)-MLD, we study the physical and chemical properties of S element and the effect of the capping layer on MLD efficiency.

Sulfur is a group number 16 element with 6 valence electrons and many allotropes, which are all insulators (S_6–S_{20}) unlike the other elements in group 16. Sulfur contributes significant covalence to bonding. As a result, AsS_x is more dominant than InS_x and GaS_x on an InGaAs surface after S-MLD.[6] Consequently, an As-rich surface may be more efficient for S-MLD. Most metal sulfides are unstable and highly reactive with O_2 and become acid. Therefore, preparing S ions, $[S_x]^{2-}$, from an acid solution is challenging and is limited to only a few solutions.[6] The common solution is ammonium sulfide $(NH_4)_2S_x$ and the associated reaction chemistry (in aqueous media) is as follows:



$$2NH_3 + H_2S + 1/2S_8 \rightarrow 2[NH_4]^+ + [S_5]^{2-}$$
$$2NH_4OH + H_2S + S_x \rightarrow 2[NH_4]^+ + [S_x]^{2-} + 2H_2O.$$

Fig. 1(a) shows the reaction energy of S with H_2 and O_2. Sulfur is chemically reactive with O_2 and becomes SO_x spontaneously, which then with H_2O moisture becomes H_2SO_x spontaneously. Hence S-MLD doping in an inert ambient such as a N_2 glove box may be an efficient way to sustain the high S dose at the InGaAs surface. However, a deionized water rinse after S-MLD dip may decrease the S dose. The thermal instability of sulfur may likewise cause non-uniformity in the S dose at the surface. The delay before depositing the capping layer should therefore be minimized. Fig. 1(b) is the reaction energy of each capping layer produced during deposition. ALD Al_2O_3 and BeO exhibit a high reaction energy, which is considered a self-cleaning reaction on GaAs and InGaAs substrates.[7,8] Because S, SO_x, or AsS_x

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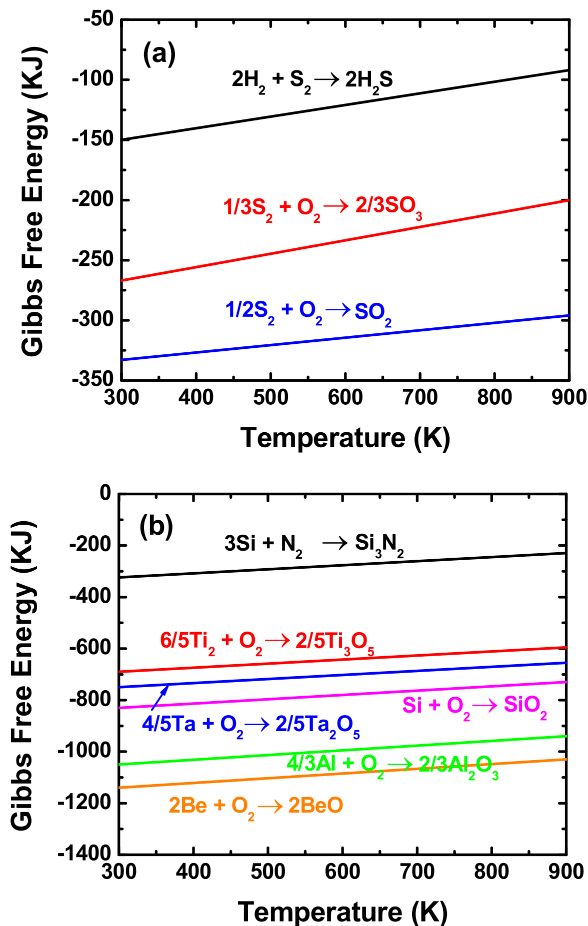


FIG. 1. Ellingham diagram for (a) standard reactions of S with O_2 or H_2, and (b) formation energy of SiN_x, SiO_x, Al_2O_3, and BeO dielectrics.

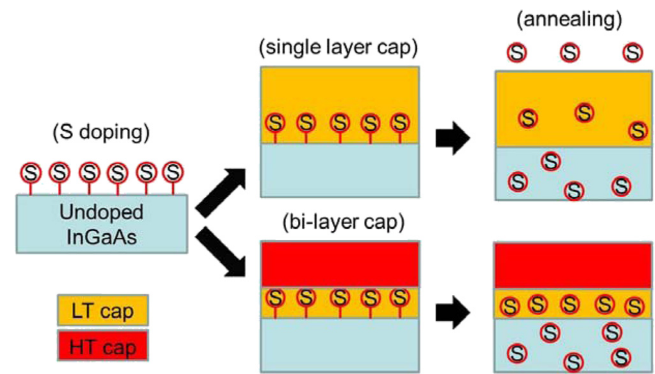


FIG. 2. Schematic diagram showing the S-MLD technique and suggested bi-layer structure.

ions at the InGaAs surface are thermally unstable, the high reaction energy during chemical deposition may precipitate desorption of S elements at the surface. SiN_x exhibits the lowest reaction enthalpy (weakest self-cleaning reaction). However, SiN_x (40.78 cm^3/mol) is much more porous because of its higher volume density than Al_2O_3 (25.8 cm^3/mol) or BeO (8.28 cm^3/mol). We also observed that the dielectric constant decreases as the deposition temperature of the capping layer decreases, indicating that porosity increased. Therefore, the best candidate for S-MLD capping may be a bi-layer structure such as a low temperature (LT) SiN_x, which sustains the S dose, and high temperature (HT) Al_2O_3 or BeO, which suppresses out-diffusion of S. It is known that gases remain in bi-layer structures longer before diffusing out, thereby improving diffusion barrier characteristics in organic light-emitting device encapsulations.[9,10] A similar bi-layer structure may therefore increase the dwelling time during S-MLD and result in more efficient dopant activation.

The schematic shown in Fig. 2 illustrates the MLD technique used here. First, $In_{53}GaAs$ epi channel substrates cleaned with diluted 1% HF are dipped in an ammonium sulfide, $(NH_4)_2S$, solution (20% in water, Sigma Aldrich) with extra sulfur (0.2 g per 15 ml of solution). Based on the above reaction chemistry, extra sulfur increases the number of S ions in an aqueous solution. The $(NH_4)_2S_x$ solution is heated up to 35 °C. The dip in solution is continued for 5–10 min. The undoped InGaAs epi substrates are then rinsed in DI water and immediately capped using a single layer (20 nm) or bi-layer (1–2 nm for LT capping + 18–19 nm for HT capping) with a total capping thickness of 20 nm. Plasma-enhanced CVD (PECVD) of SiN_x or SiO_2 or ALD Al_2O_3 is used for a LT (30 to 150 °C) capping layer. For a HT capping layer, ALD Al_2O_3 or BeO is grown at 250 °C. For ALD Al_2O_3 and BeO, trimethylaluminum and diethylberyllium, respectively, are used. H_2O or O_2 is used as an oxygen source for both oxides. NH_3+N_2 gases for PECVD SiN_x and NO_2 + N_2 gases for PECVD SiO_x were used, respectively, with a minimized plasma power of 30 W. The deposition rates were measured using ellipsometry with a frequency and angle range of 350–1300 nm and 45°–75°. With higher plasma power, the deposition rate of the capping layer increases but the S dose decreases (data is not shown here). At a plasma power below 30 W, no deposition is observed. Thermal annealing is then performed at 700 °C for 30 s to drive S atoms into the InGaAs epi channel. HL5500 system for Hall measurement is used to determine the surface sheet resistance (R_s), effective carrier density and mobility with permanent magnet of 500 G, constant current ranging from 0.1 μA to 20 mA, and high input impedance voltmeter covering to 1 V. To confirm the accuracy of Hall measured Rs value, 4 probe measurements were performed. Both measurement techniques show similar results of R_s.

In Fig. 3(a)), a low growth temperature generally results in low R_s, indicating more sulfur has been incorporated into the undoped $In_{53}GaAs$ epi layer. H_2O-based ALD Al_2O_3 produces better R_s than O_2-based ALD Al_2O_3. This may be due to the high reactivity of O_2 molecules with S elements as seen in Fig. 1(a). Comparing single layers of ALD Al_2O_3 and PECVD SiO_x (or SiN_x) at the same deposition temperature, ALD Al_2O_3 exhibits lower R_s. This may be due to the absence of plasma or the less porous nature of of ALD Al_2O_3. However, because the available ALD precursor line is limited, ALD SiN_x or SiO_x could not be tested. As expected from Fig. 1(b), bi-layer structures such as SiO_x (or SiN_x)/Al_2O_3 (or BeO) clearly have lower R_s than single layer structures such as SiO_x or SiN_x (Fig. 3(b)). Compared to SiO_x, SiN_x generally exhibits better R_s on both single and bi-layer structures, which may be due to the lower reaction energy produced during SiN_x deposition. The R_s of SiN_x/BeO bi-layer structure is slightly better than that of SiN_x/Al_2O_3

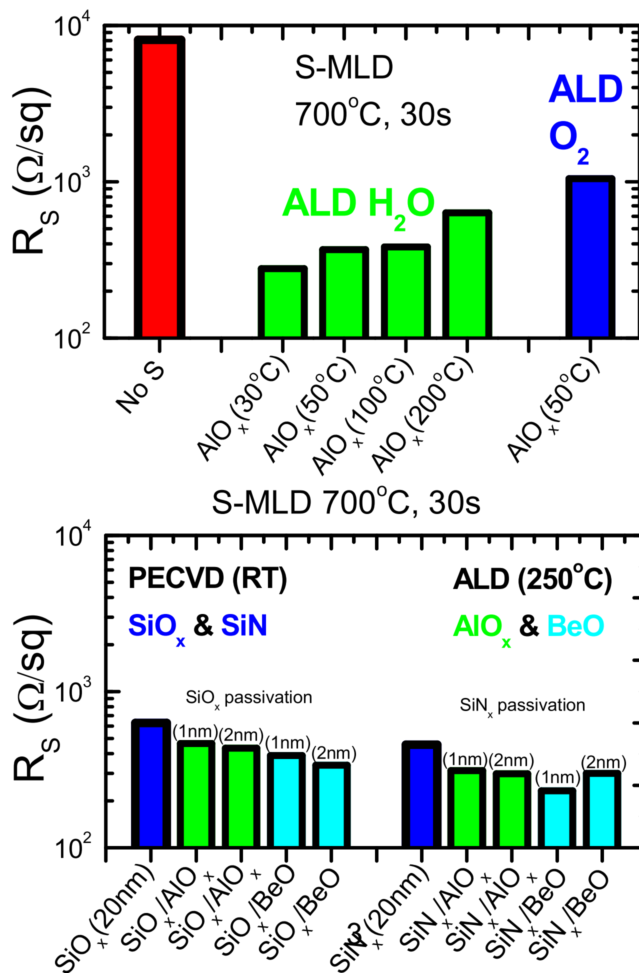
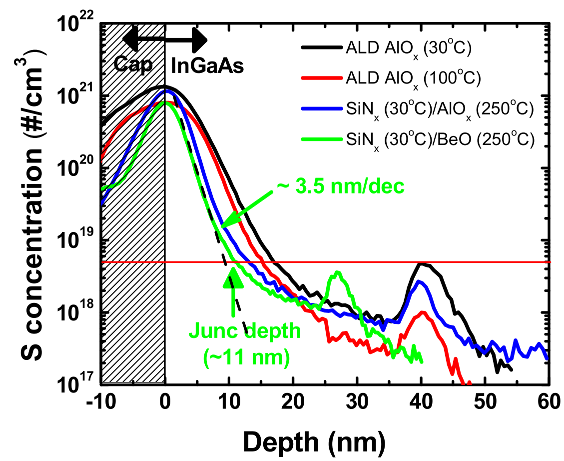


FIG. 3. Summary of surface sheet resistance with various capping dielectrics and growth conditions.

bi-layer structures. It is known that gas (including oxygen or sulfur) diffusion through a thin film is proportional to the number of pinholes and the pinhole size in the film. Generally, materials of smaller molecular sizes have relatively smaller pinhole sizes. The smaller pinholes cause more collisions between oxide and gas molecules during diffusion, inhibiting permeation. Therefore, ALD BeO may more efficiently prevent S from diffusing out than ALD Al_2O_3 since BeO has a lower volume density. BeO is already well-known in industry as gas diffusion barrier. Fig. 4 is the secondary ion mass spectrometry (SIMS) analysis and summary of Hall measurements. Bi-layer caps have shallower and more abrupt junctions than single layer caps. The SiN_x/BeO bi-layer capping, compared to single layer cap, exhibits the best results with a surface sheet resistance of 232 Ω/sq, junction depth of 11 nm, dopant profile abruptness of 3.5 nm/dec, electrically active sulfur concentration of $4.9 \times 10^{19}/cm^3$ ($=1.34 \times 10^{13}/cm^2$), and 3 times higher activation efficiency without significant transient-enhanced dopant diffusion. Due to the non-uniformity of initial S dose, Al_2O_3(30 °C) single layer capping shows the highest dopant drive in, but its junction depth also much increased, compared to that of bi-layer capping. Therefore, if Al_2O_3(30 °C) single layer capping has around 10 nm junction depth, it definitely has less dopant drive in.



Capping layer	Temp [°C]	R_s [Ω/sq]	n_s [#/cm²]	Activation Efficiency [%]
Al_2O_3	30	278	1.60×10^{13}	2.6
Al_2O_3	100	382	9.58×10^{12}	2.3
SiN/ Al_2O_3	30/250	297	1.03×10^{13}	2.7
SiN/BeO	30/250	232	1.34×10^{13}	7.0

FIG. 4. SIMS profile of S-MLD for a single Al_2O_3 (30 °C, 100 °C), and bi-layer structures, SiN_x/Al_2O_3 and SiN_x/BeO.

In summary, we have studied the reactivity of S elements and the reaction energy of capping materials to suggest an optimized scheme, a bi-layer structure, targeted at high S-MLD efficiency. From this study, we have found that S-MLD is sensitive to the capping conditions such as the capping layer growth temperature and precursor reaction energy at the channel surface. SiN_x/BeO, one of the bi-layer structures, may be a useful solution to improve the activation efficiency of S-MLD to realize nanoscale III–V devices.

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