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Featured Letter

Introducing gallium in silicon and thin film polysilicon using self assembled monolayer doping

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ABSTRACT

Monolayer Doping (MLD) is a technique involving the formation of a self-assembled dopant-containing layer on the substrate. The dopant is subsequently incorporated into the substrate by annealing, forming a diffused region. Following MLD, samples were capped with silicon dioxide and rapid thermal annealed (RTA). In this work, gallium doping using MLD has been demonstrated. Gallium containing compound Tris (2,4 pentanedionato) gallium(III) was synthesized, and shown to be suitable for monolayer doping silicon substrates and deposited thin film polysilicon. Secondary ion mass spectroscopy (SIMS) and spreading resistance probe (SRP) measurements were performed to determine the dopant profiles and dopant electrical activation. These results showed that a dose of $1.6*10^{15}$ atoms/cm^2 was received, and the gallium dopant produced a 0.2 μm junction in *n*-type silicon. For polysilicon, the entire 0.4 μm film was evenly doped, with a concentration greater than 10^{19} atoms/cm^3 throughout.

1. Introduction

There is a demand for new doping techniques, due to the ongoing scaling down of semiconductor device dimensions with 3D architectures that is motivated by Moore's Law [1]. Current wafer doping methods include ion implantation [2], thermal diffusion [3,4], and monolayer doping (MLD) [5,6]. Herein we focus on MLD, a method that relies on the formation of dopant monolayers through a chemical reaction between the hydrogen-terminated substrate surfaces and dopant molecules. MLD is promising as it is a non-damaging, conformal, and patternable doping method, capable of producing ultra-shallow junctions [7]. Additionally, this technique can be applied to a range of thin films and substrates such as silicon, germanium, InAs, InP, GaAs, and InGaAs [8]. Silicon MLD has been shown to be a viable method of phosphorus and boron doping, and previous work from this group has utilized such dopants for the creation of N + P diodes [5,9].

In this work, gallium doping via MLD has been explored. In recent years, gallium has been gaining interest, particularly in the solar industry where light-induced degradation (LID) of boron is a concern [10,11]. Given the stability of gallium, it is the most promising group 13 element to address LID [12]. Additionally, gallium as the p-type dopant in poly-Si:Ga/SiO2 passivated contacts in *n*-type Si solar cells has shown promising results in overcoming the passivation limitation of the poly-Si:B/SiO2 [13].

Monolayer doping originally relied on a silicon radical reacting a functional alkene group on the dopant molecules, and much of the literature relies on such a mechanism [5–8,10,11]. This reaction mechanism is complex and limits dopant types. In this paper, we present data showing the doping of silicon and polysilicon with gallium can be accomplished using a hydrogen-bonding mechanism between the dopants and the hydrogen-terminated surface. Such a mechanism has been previously reported and allows many new dopant compounds to be considered [14].

2. Materials and methods

A gallium acetylacetonate dopant complex was synthesized, as described in Fig. 1a and supporting information. This structure was characterized for yield, purity, and structural identification, using fourier transform infrared spectroscopy (FTIR), Raman, and proton

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NMR (Table S1). Commercial Tris(2,4 pentanedionato)gallium(III) (TCI chemicals) was used as a comparison standard. H NMR samples were dissolved in deuterated chloroform. Thermogravimetric analysis (TGA) was conducted on the gallium samples increasing from room temperature to 400 °C at the rate of 5 °C/min.

For gallium, a dopant solution was created by dissolving four grams of Tris(2,4 pentanedionato)gallium(III) in 300 mL mesitylene, and sparged with argon for 15 min. The wafers, (1 0 0) *n*-type silicon with a resistivity of 2 Ω.cm, were etched in 10:1 HF BOE solution for 20 s to remove the native oxide layer, rinsed in water, and dried (Fig. 1b). For polysilicon sample preparation 0.5 μm of furnace oxide was grown, followed by the deposition of 0.4 μm of polysilicon via Low-Pressure Chemical Vapor Deposition (LPCVD), with conditions of 300 mTorr of pressure, at 610°Celsius, for 60 min. For both silicon and polysilicon, MLD was completed under an argon atmosphere, by submerging the wafers in the gallium solution for two to four hours at 125 °C in a reaction chamber previously detailed [9]. After MLD the wafers were removed, washed with toluene, acetone, methanol, and water, sequentially, and dried using nitrogen. Following the MLD, the samples were capped with 70 nm of silicon dioxide by Plasma Enhanced Chemical Vapor Deposition (PECVD). The samples were activated by RTA at 1100 °C for 10–20 s in a nitrogen environment and etched.

3. Results and discussion

With high yield and purity, gallium acetylacetonate complex was synthesized. Spectroscopic evidence matches the results obtained from a commercial standard of gallium acetylacetonate (Table S1). This synthetic version of the dopant identified a reaction pathway to produce other gallium dopants, which will be the focus of future work. Thermal Gravimetric Analysis (TGA) in a nitrogen atmosphere was conducted on the synthesized compound and the standard, which were nearly identical in the comparative thermal decomposition profiles (Table S1, Fig. S1).

Secondary ion mass spectroscopy (SIMS) was performed to determine the concentration and the profile of the introduced dopant. The results show that Tris(2,4 pentanedionato)gallium(III) (Fig. 2a) was able to produce a concentration greater than 10^{20} atoms/cm^3 in the top 37 nm of the substrate. A total dose of $1.6*10^{19}$ atoms/cm^2 was received. To assess electrical activation spreading resistance probe (SRP) measurements were performed. The sheet resistance was measured as 865 O/square. For SRP samples are beveled exposing various depths of the sample. Measurements are taken with a 2-point probe, which are compared to NIST calibration standards to determine the resistivity [15]. The resistivity (Fig. S2) is converted to carrier concentration (Fig. 2b) using published mobility values. The SRP results show that the top 0.2 μm of the substrate was p-type, indicating that a shallow junction was created. The SIMS and SRP results show that there is some inactive gallium at the surface, however, after the top 0.05 μm, electrical activation is higher. Solid solubility of Ga is ~ $2*10^{19}$ atoms/cm^3 at the temperature used in annealing [13]. Near the junction, the SIMS profiles also deviate from SRP due to their different measuring mechanisms [17].

Results from SIMS show that MLD utilizing Tris(2,4 pentanedionato) gallium(III) is capable of complete and uniform doping of the deposited polysilicon, with a concentration greater than 10^{19} atoms/cm^3(Fig. 3a). The total dose received was $3.2*10^{17}$ atoms/cm^2. To convert measured resistivities to the carrier concentration (Fig. S3) a constant carrier hole mobility of 13 cm^{2}V^{-1}s^{-1} was assumed based on published carrier mobility values of p-type dopants in thin-film polysilicon [16]. The SRP profiles show that the carrier concentration of Ga (Fig. 3b) remains

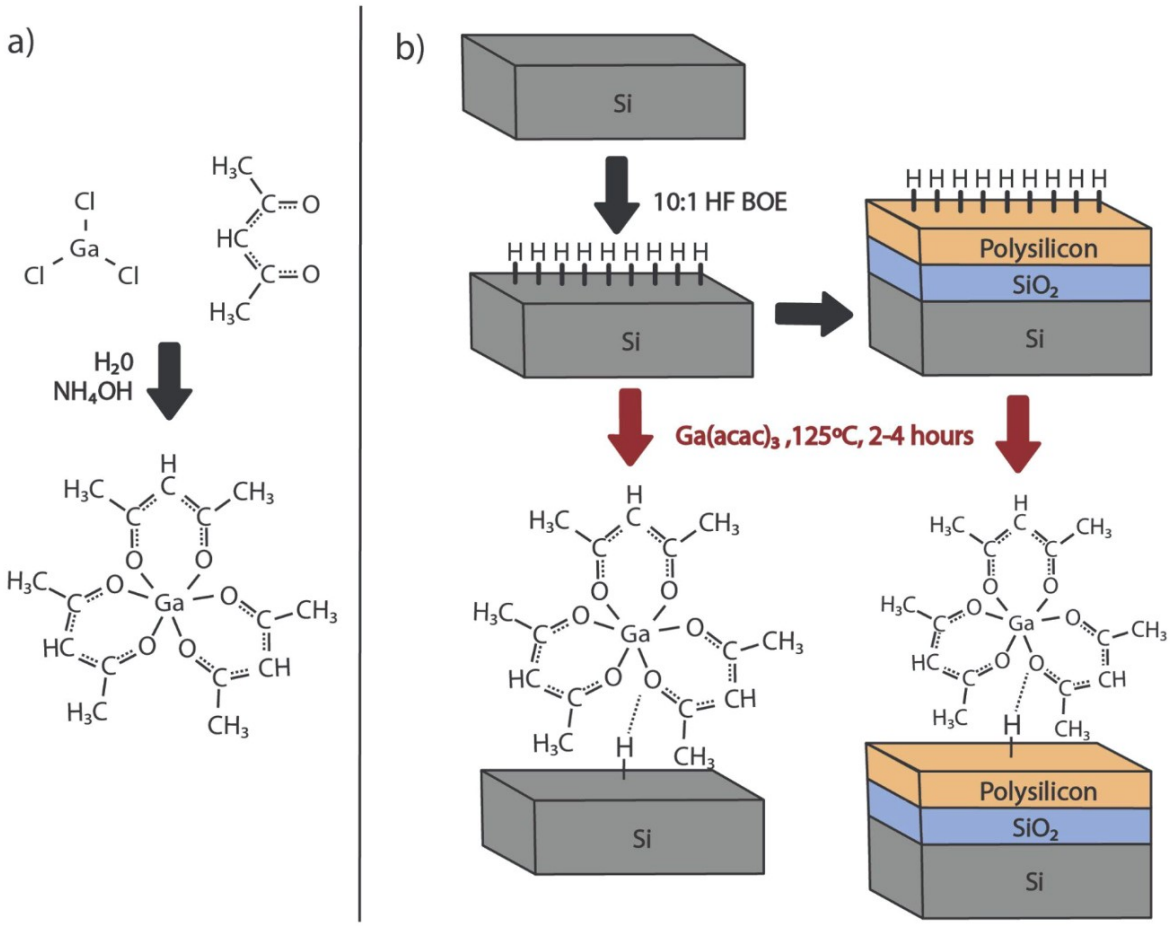

Fig. 1. a) Synthesis of Tris(2,4 pentanedionato)gallium(III) and b) monolayer formation processing steps.

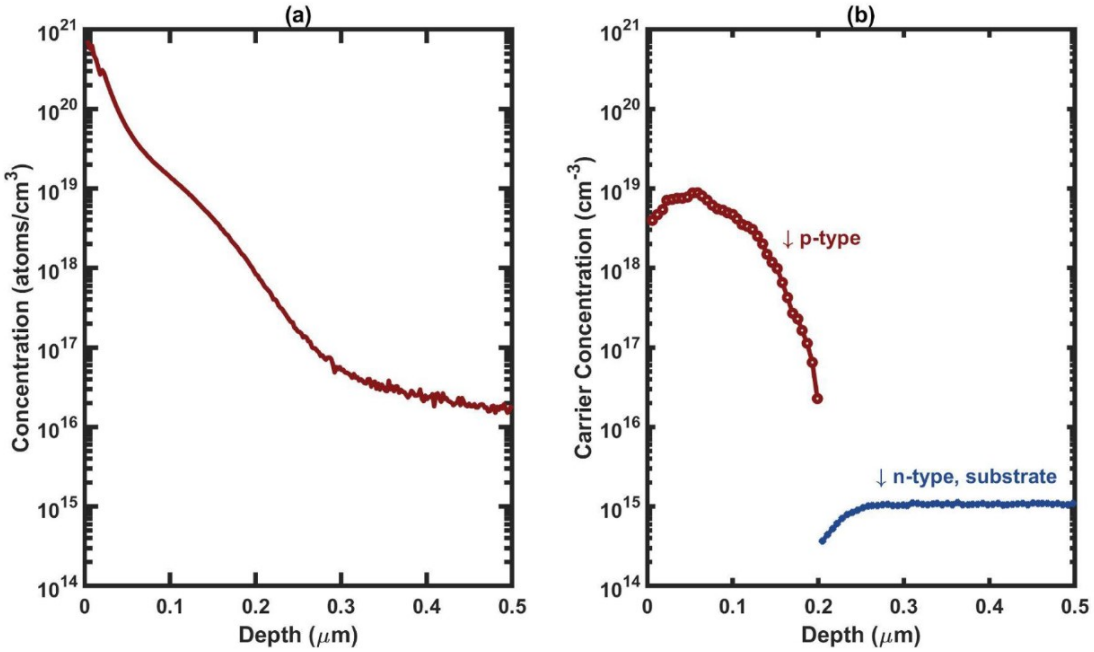

Fig. 2. a) Dopant concentration from SIMS analysis and b) carrier concentration from SRP measurements for gallium doped silicon.

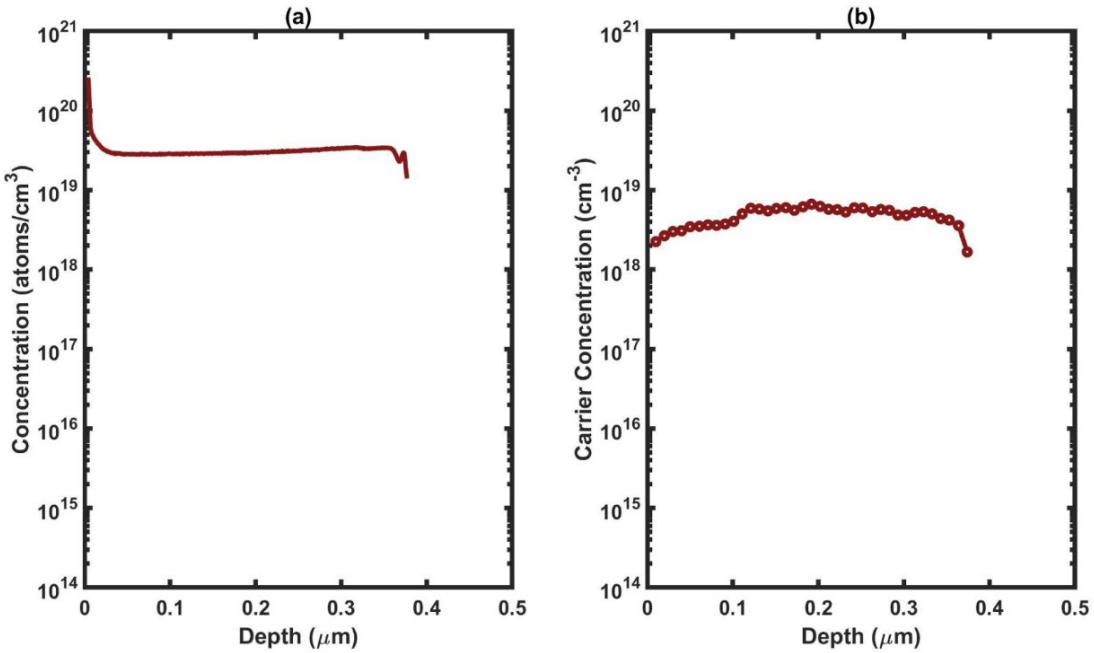

Fig. 3. a) Dopant concentration from SIMS analysis, b) carrier concentration from SRP measurements for gallium doped thin film polysilicon.

constant throughout the entire depth of the film. While the dose received in polysilicon was two-hundred times larger than what was received in silicon, 20 % of the dose received was electrically active. The greater dose in polysilicon is enabled by the grain structure and higher diffusion through grain boundaries [18].

4. Conclusions

Gallium doping in silicon and polysilicon using MLD has been demonstrated using Tris(2,4 pentanedionato)gallium(III) compound followed by rapid thermal anneal. Supporting the hydrogen bonding mechanism [14]. In silicon, this gallium compound resulted in a junction depth of 0.2 μm and a dose of $1.6*10^{15}$ atoms/cm^2. For thin film polysilicon, the thin film was evenly doped throughout, with the carrier concentration greater than $5*10^{18}$ atoms/cm^3. These results show that monolayer doping offers a promising alternative to dope polysilicon films for thin film electronics applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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