Room-temperature plasma doping without bias power for introduction of Fe, Au, Al, Ga, Sn and In into Si

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Abstract It is demonstrated by use of secondary ion mass spectroscopy that some impurities, including Fe, Au, Al, Ga, Sn and In, can be doped into Si wafers with depths of tens nanometer but quite high densities in radio frequency (RF)-excited plasma without any bias power at room temperature. This process is referred to as plasma doping without bias (PDWOB). In PDWOB, the quantity and depth of an impurity doped into the Si wafer depend on the character of the impurity, power of the RF that excites the plasma and the processing time of the PDWOB. The good fitting of the complementary error function distribution with the experimental data of the concentration distributions of the impurities doped into Si wafers indicates that PDWOB is a result of room-temperature diffusion of impurities in Si stimulated by vacancies and Si self-interstitials induced by plasma. The application prospects of the PDWOB, including doping ultra-thin films, ultra-shallow junctions and two-dimensional materials, are emphasized.

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1 Introduction

In semiconductor industry and study, commonly used methods for doping impurities into Si bulk materials include thermal diffusion and ion implantation. Thermal diffusion needs high temperature and generally quite long time, in which case contamination from environment easily occurs. For ion implantation, ultra-shallow implantation depth, for example, an ultra-shallow range of tens of nm, is generally difficult to realize and the equipment is too expensive to be widely configured and some kinds of defects produced by ion implantation in target material are remained even after thermal annealing [1, 2]. Plasma immersion ion implantation (PIII) has been reported and used [3–5]. In the plasma immersion ion implantation process, besides the plasma excited by radio frequency (RF), a bias RF power is applied and then a high-voltage sheath forms at the surface of the target material and ions in the plasma are accelerated and implanted into the target material [6]. As a result of the existence of the high-voltage sheath, an evident part of the target material is etched during PIII, so it cannot be applied to doping of ultra-thin films and ultra-shallow junction devices.

In this paper, it is demonstrated by use of secondary ion mass spectroscopy (SIMS) that some impurities, including Fe, Au, Al, Ga, Sn and In, can be doped into Si wafers with ultra-shallow depths but quite high densities in a RF-excited plasma without any bias power (PDWOB) at room temperature. In the PDWOB, both a impurity source and a Si target material are placed in the plasma. In the PDWOB, no etching effect occurs for the Si target material. The doping depths of impurities in the PDWOB are usually in a range of tens of nanometer, which depends on the kind of the impurity and power of the RF which excites the plasma; therefore, the PDWOB can be applied to doping of ultra-

thin films and ultra-shallow junction devices and two-dimensional materials.

It has been found that the novel doping method of plasma doping without bias power cannot be applicable for all kinds of elements in the periodic table. To evaluate the novel method, it is essential to know what kinds of elements can be doped into Si at room temperature by the method and what cannot be no matter what functions these elements play in Si. We have tried our best to give the answers. Secondary ion mass spectroscopy, which is a very expensive testing method, may be the only technique, which can solve the problems. So far, it has been found that Fe, Au, Al, Ga, Sn and In could be and As and Ge could not be doped into Si at room temperature by the method. Some of the above-mentioned elements are favorable in Si. For example, Au can be introduced into the Si switching diodes, switching transistors and thyristors to improve their switching speed [7, 8]. Ga-doped Czochralski silicon (CZ–Si) crystal is a promising material for Si-based solar cells, with high minority carrier lifetime and no light-induced degradation [9]. And the others in Si are likely to have some use in the future.

2 Experimental details

The inner wall and the substrate of the plasma reaction chamber were coated with high-purity quartz (99.999%) and Si wafers, respectively, avoiding contamination of the impurities from the inner wall and the substrate of the chamber.

In consideration of high cost and quite difficult acquisition of Si nanometer thin film, crystalline Czochralski-grown Si (110) wafers (p-type, 2Ω cm, $625 \mu m$ thick) instead of Si ultra-thin films are used in our experiments. All of the Si samples were cut into 1×1 cm^2. A piece of stainless-steel sheet, gold foil, aluminum foil, tin wafer and indium ingot and GaAs and germanium wafers were employed as the solid doping sources of Fe, Au, Al, Sn, In, Ga, As and Ge, respectively. Before the PDWOB, a definite solid doping source and Si wafers were properly washed and blown dry with N_2 gas. The solid doping source was placed near the center of the substrate of the chamber. Helium with a gas flow of 22.4 sccm was piped into the chamber, and the RF power was inductively coupled to the working gas to generate plasma. Here, no bias RF power was applied in the PDWOB. The pressure in the chamber ranged from 3E-2 to 6E-2 Pa. Compared with the ambient temperature, the temperature rise in the chamber during the PDWOB was less than 8 °C for 750 W and 1 °C for 50 W, measured by both infrared thermometer and thermistor thermometer.
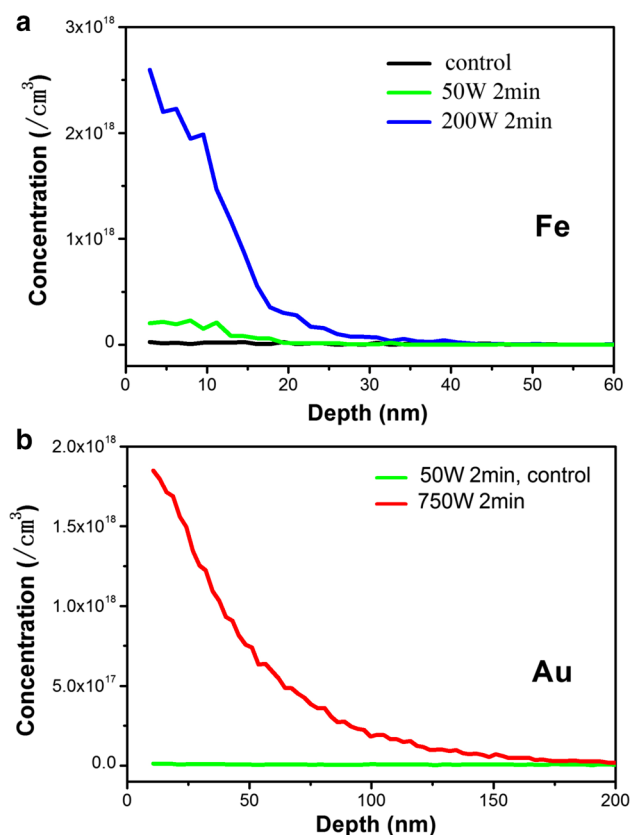
The concentration distributions of Fe and Au in Si wafers were measured by secondary ion mass spectroscopy (SIMS) (Cameca IMS-4fE7, France) in China Electronics Technology Group Corporation No. 46 Research Institute 3 days after the PDWOB. The SIMS measurements for Al, Ga, Sn, In, As and Ge were taken on IONTOF V (USA) in Evans Analytical Group about 1 week after the PDWOB. The surface topography and roughness of the Si wafers after plasma treatment were measured by use of atomic force microscope (Veeco Di MultiMode V,USA).

In the SIMS measurement of Au distribution in Si, Cs^+ with energy of 5 keV was used as the primary ions and in that of Fe distribution in Si, O_2^+ with energy of 15 keV was used as the primary ions. For Al, Ga, Sn, In, As and Ge, O_2^+ with energy of 1 keV was used as the primary ions. In consideration of the matrix effect and the surface transient effect of SIMS, both of which make the concentration distributions within the top surface region of Si inaccurate, the concentration data of Au within 10 nm and those of Fe, Al, Ga, Sn, In, As and Ge within 2 nm from the top surface are omitted.

3 Results

Figure 1 shows the concentration distributions of Fe and Au in Si wafers after the PDWOB of Fe and Au into Si wafers with different RF powers. The time of the PDWOB operation was 2 min. It can be seen in Fig. 1a that the Fe concentration of the control sample without plasma treatment is near or under the SIMS detection limit of 1E16/cm^3 for Fe. With increasing RF power, the surface concentration of Fe increases and the doping length expands. The doping length is defined as the depth of the region where the concentration of the impurity is over the SIMS detection limit. At the top surfaces of the Si wafers which were doped in PDWOB at RF power of 50 W, the concentration of Fe is an order of magnitude higher than 1E16/cm^3, while that of Au is near the Au detection limit of 1E16/cm^3, as shown in Fig. 1b. When the RF power was enhanced up to 750 W, the Au concentration at the surface of Si increased to 1.8E18/cm^3. The doping length reaches about 150 nm for Au. Figure 1 indicates that Fe and Au have been introduced into Si by PDWOB.

Figure 2 shows that the concentrations of Al, Ga, Sn, In, As and Ge in the control samples are too low to be identified. After PDWOB with RF power of 750 W in 2 min, Al was introduced into Si wafer with a high surface concentration of 6E20/cm^3. The concentrations of Ga, Sn and In in the surface regions of Si wafers increase drastically after PDWOB, which indicates that Ga, Sn and In could also be introduced into Si wafers by PDWOB. However, as for As and Ge, the surface concentration of them in the Si wafers after PDWOB in the same condition is still near or

Fig. 1 SIMS results for the distributions of Fe and Au in Si wafers after PDWOB Fe and Au, respectively, into the Si wafers in 2 min, and the PDWOB is excited by RF powers indicated. Both the concentrations of Au in the control sample and in the Si wafer after Au PDWOB excited by 50 W RF are under the detection limit

under the detection limit, as is the case with the control sample. It reveals that not all kinds of elements in the periodic table can be introduced into Si by PDWOB.

The surface topography and roughness of the plasma-treated Si wafers were examined by using atomic force microscope (AFM), as shown in Fig. 3. It is supposed that the surface damage induced by plasma can be indirectly reflected by the surface roughness of the Si sample. The surface roughness value Rq of the Si sample treated by He plasma with RF power of 50 W in 2 min is 0.16 nm, which is nearly equal to that of the control sample, while the surface of the Si sample treated by He plasma with RF power of 750 W in 2 min becomes a little rougher (Rq = ~0.53 nm), which indicates that a light surface damage is induced by PDWOB. After the PDWOB (750 W, 2 min), the etched-out thickness of the Si wafer was only ~0.5 nm; for comparison, the etched-out thickness of the sample which was treated by 750 W He plasma using a moderate bias power of 100 W in 2 min was ~22 nm.

A study on the elimination of the surface damage induced by plasma has been conducted. It has been found that after rapid annealing (950 °C, 15 s), the Rq value of the sample treated by 750 W plasma for 2 min can be reduced from 0.53 to 0.19 nm, which is quite close to the Rq value of the control sample. As a consequence, it can be speculated that the surface damage produced by plasma can be largely eliminated by rapid annealing.

4 Discussion

During the PDWOB, an RF oscillating electric field is generated in the gas region through the use of magnetic induction. At low vacuum, the residual electrons in the chamber are heated by the combined effects of the electric field and scattering with Helium atoms. When electrons obtain enough kinetic energy, which is higher than the first ionization threshold of He atom, collisions lead to ionization, yielding additional free electrons and He^+ ions and both are heated in turn. Consequently, plasma is formed.

On the one hand, the plasma induces point defects in the surface region of Si wafers. It has been found that the formation energy of a vacancy and self-interstitial in Si is in a range of 3–5 eV [10], while the energy of He ions or electrons in the plasma with the RF power of 750 W is estimated more than 30 eV [11]. Therefore, it is considered that vacancies and self-interstitials in Si are produced near the surface during the PDWOB. Both of vacancy and Si self-interstitial have high mobility in Si even at low temperature [12–15]. On the other hand, the plasma ablates some atoms of the outer layers of the solid impurity source. These ablated free impurity atoms or ions, which are labeled as IAs, get into the He^+-electron plasma and quickly obtain kinetic energy.

The IAs may enter into the Si wafer in one of the two ways as follows: For some kinds of IAs, whose radius are small, such as Fe and Ga, they can get into the Si wafer through the interstices at the top surfaces of Si wafers or through the channeling effect. For the other IAs, whose radius is large, such as Au, they firstly absorb on the top surface of Si wafer. When a vacancy induced by plasma moves next to the absorbed IA, the IA can enter into the Si wafer by jumping into the vacancy.

The initial energy of IAs getting into Si via the interstices or vacancies is higher than their energy under thermal equilibrium at room temperature in Si. After a short movement and collision with lattice atoms and the interstitial–substitutional exchange, IAs reach thermal equilibrium state. For IAs that enter into Si through the interstices but are predominantly substitutionally dissolved under thermal equilibrium, they stay on substitutional sites after a short-range transport in the interstitial, labeled as IA_s, while for IAs that get into Si in the second way, i.e., with the help of vacancies, but are dissolved on interstitial sites, which are energetically favored, they fall off into the interstitials from the substitutional sites, labeled as IA_i.
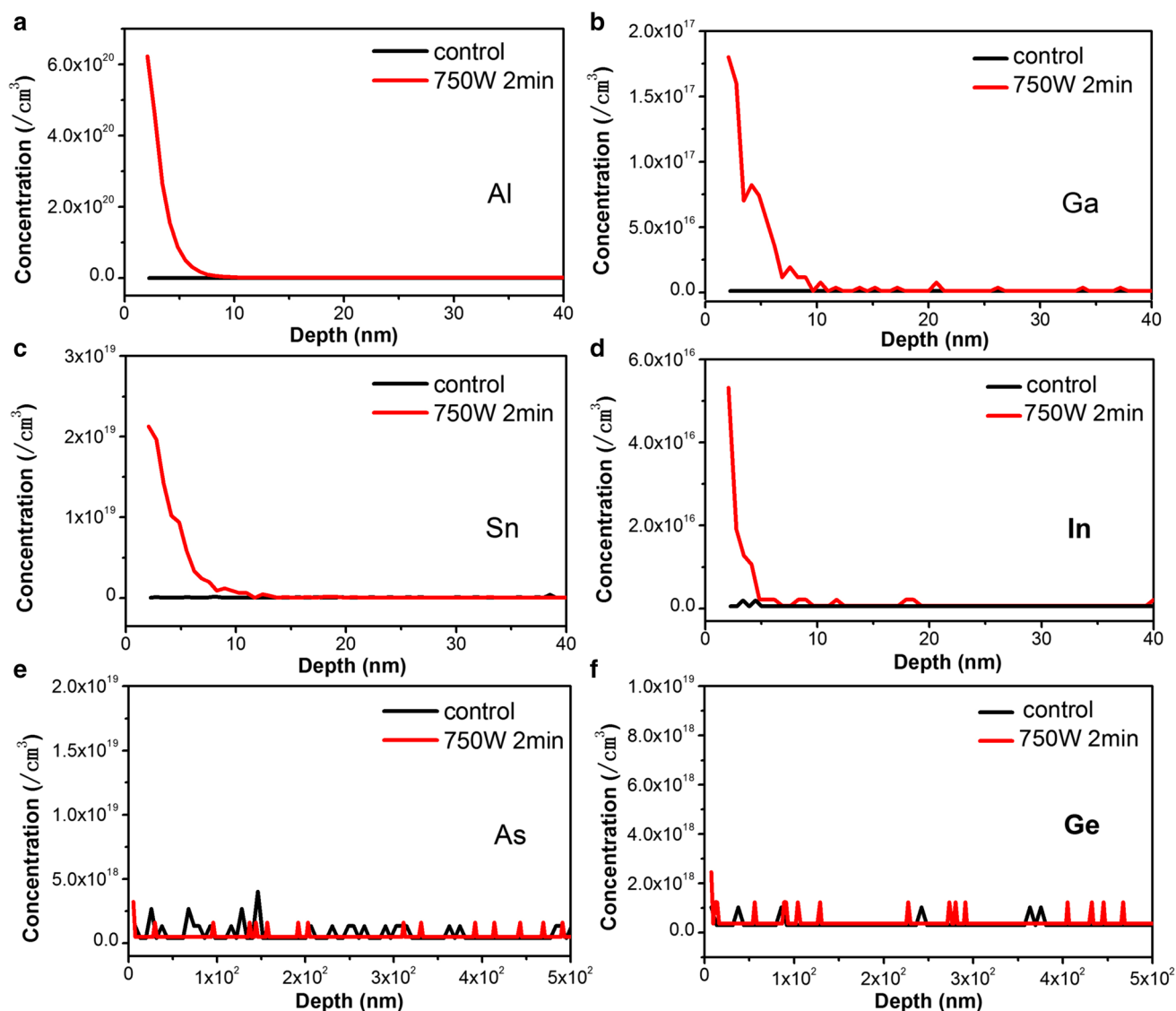
Fig. 2 SIMS results for the concentration distributions of **a** Al, **b** Ga, **c** Sn, **d** In, **e** As and **f** Ge in Si wafers before and after PDWOB (750 W, 2 min)

Fig. 3 AFM height images of sample a (control), sample b (50 W 2 min PDWOB) and sample c (750 W 2 min PDWOB). The length scale is 5 micron. The surface roughness value Rq of **a**, **b** and **c** is 0.15, 0.16 and 0.53 nm, respectively
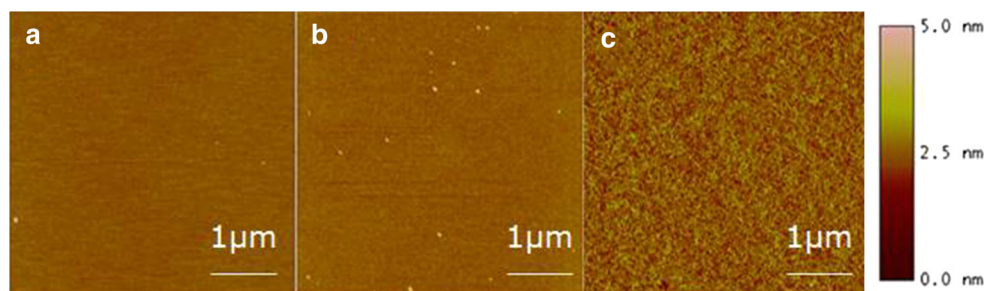
According to Fick's second law, when the surface concentration and diffusion coefficient D are constant, the concentration distribution of impurity diffusing in Si should be the complementary error function distribution:

$$N(x,t) = N_s \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\alpha^2} d\alpha \right) \qquad (1)$$

where x, t and N_s denote the depth from the surface, the diffusion time and the surface concentration of the impurity, respectively. During the PDWOB, suppose that N_s is a constant when the plasma-impurity-Si wafer system reaches thermal equilibrium. As shown in Figs. 4 and 5, the complementary error function shown in Eq. (1) fits quite well with the experimental data of the concentration distributions of the impurities doped into Si wafers by PDWOB. As a consequence, it is considered that PDWOB is really a room-temperature diffusion process. However, it is well known that the room-temperature diffusion of impurity in Si is too slow to be observed. Therefore, vacancies and Si self-interstitials induced by plasma play a

Fig. 4 Complementary error function distribution fitting results of the concentration distributions of Fe and Au in Si wafers after the PDWOB of Fe and Au, respectively, into Si wafers in 2 min. The PDWOB is excited by RF powers indicated

key role in the room-temperature diffusion of the impurities stated above in Si.

Generally, IA can diffuse faster in the interstitial than in the substitutional because motion of IA_s in Si needs two kinds of activation energies: the energy of formation of a native defect, i.e., vacancy [16] or Si self-interstitial [17], and the energy of migration of IA_s [18]. In this case, vacancies and self-interstitials have been made by plasma, and the diffusion of IA_s just requires to climb over the barrier of migration, which is beneficial to the room-temperature diffusion of IA_s. IA_s may diffuse in Si via two possible mechanisms. The first one is that, when a vacancy from the surface moves next to IA_s, IA_s can jump into the vacancy and diffuse further in Si via the subsequent vacancies in the same way. The second one is the so-called kick-out mechanism [19]. Consequently, the room-temperature diffusion of IAs is accelerated. For example, Au, which is known as one of the fastest diffusers in Si, can diffuse just 10 nm in 10 days at room temperature [20], and the room-temperature diffusivity of Au in Si is calculated to be about 2.9E-20 cm^2/s. However, the room-temperature diffusion length of Au in the PDWOB is more than 150 nm after PDWOB in just 2 min, and the fitting result of the room-temperature diffusivity of Au in Si in the PDWOB is 9.9E-14 cm^2/s. It can be seen in Fig. 4 that the N_s of Fe for the Si wafer treated by plasma with 200 W is about ten times higher than that for the Si wafer treated by plasma with 50 W. The density of plasma is positively dependent on the RF power of plasma [21]; therefore, the quantity of vacancy and self-interstitial and IAs increases with increasing the RF power. As a consequence, the higher the RF power is, the higher the N_s is. The fitting result of the room-temperature diffusivity of Fe in the Si wafer after PDWOB with 50 W is 8.5E-15 cm^2/s, which is close to that in the Si wafer after PDWOB with 200 W, which is 6.1E-15 cm^2/s. To our best knowledge, little study about the room-temperature diffusion of Al, Ga, Sn and In in Si has been reported. By fitting the SIMS results of the concentration distributions of Al, Ga, Sn and In in Si after PDWOB with RF power of 750 W with the complementary error function distribution, the room-temperature diffusivity of Al, Ga, Sn and In in Si is obtained, namely 1.49E-16, 3.73E-16, 4.22E-16 and 8.25E-17 cm^2/s, respectively.

It is well known that the room-temperature diffusion coefficients of most elements in Si are very small. In our method of plasma doping without bias power, with the help of point defects induced by plasma, some impurity atoms or ions are in a state where their diffusion coefficients are greatly increased, and their diffusion in Si can occur even at room temperature. However, for some impurities in Si, their room-temperature diffusion coefficients are still very small even stimulated by plasma, because their diffusion coefficients are originally much too small without plasma
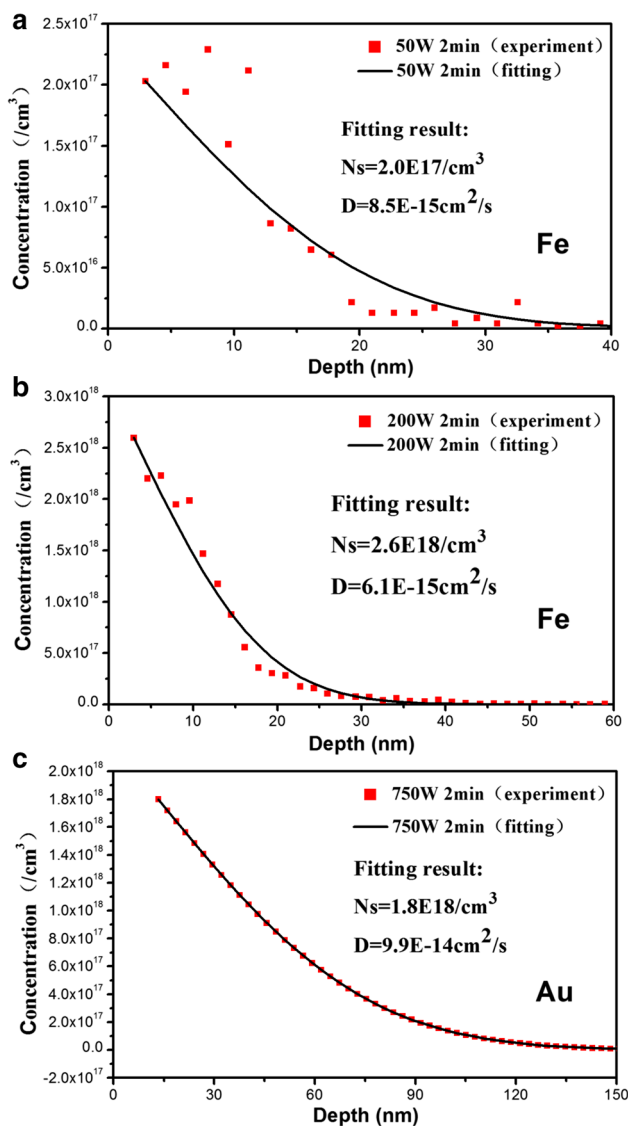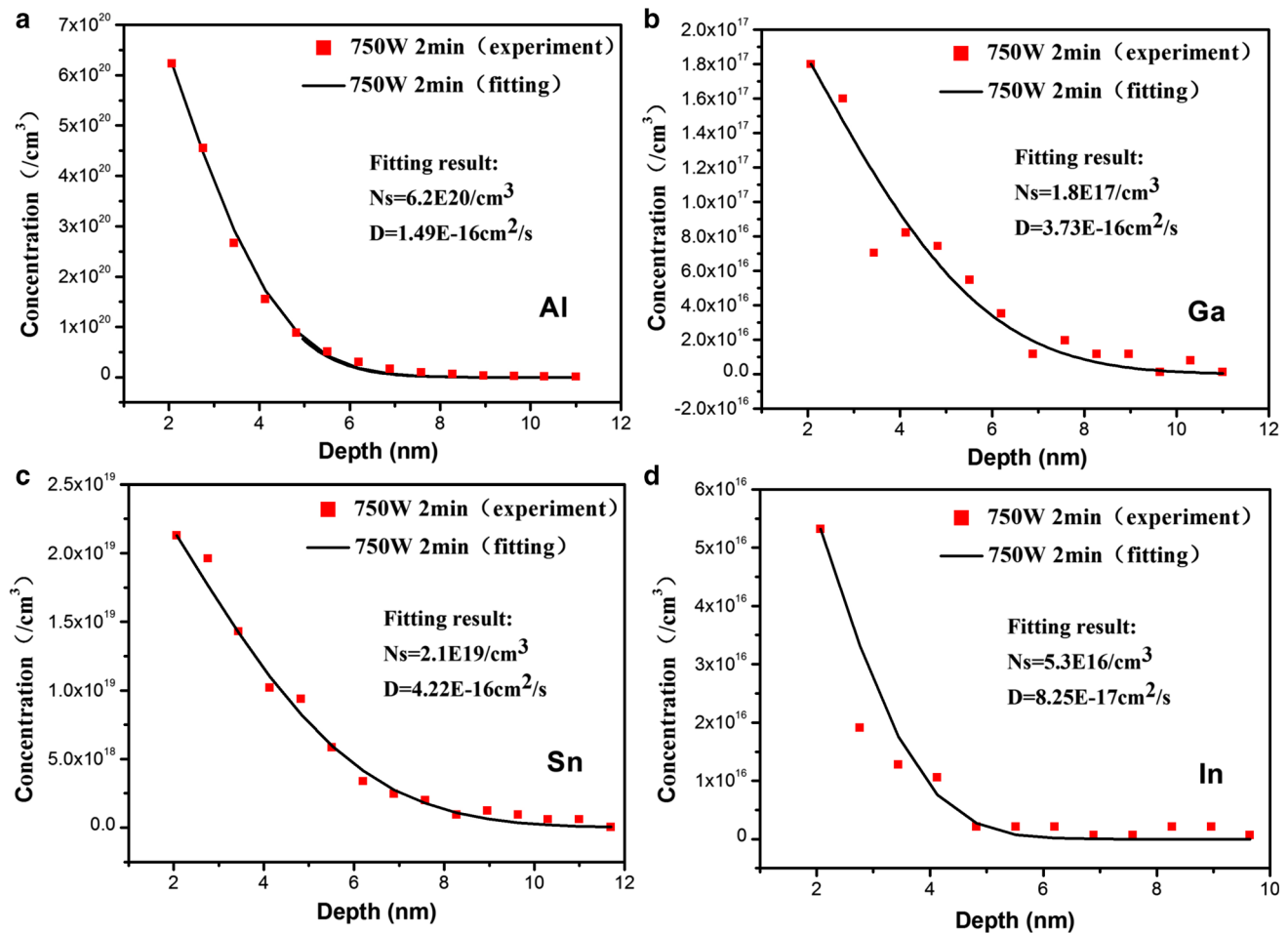
Fig. 5 Complementary error function distribution fitting results of the concentration distributions of Al, Ga, Sn and In in Si wafers after the PDWOB (750 W) of Al, Ga, Sn and In, respectively, into Si wafers in 2 min

stimulation and/or the magnifying multiples of their diffusion coefficients are not large enough during plasma process. As and Ge may belong to this situation.

This room-temperature PDWOB of impurities into Si may have many applications in silicon science and industry. For silicon nanometer thin films and silylene, PDWOB may be an appropriate and effective doping method. Besides, this method is also hopeful to be applied to producing ultra-shallow p–n junctions with high doping concentration in a simple and convenient way. Compared with PIII, this method avoids the etching and lattice damage of Si target material and can obtain ultra-shallow doping depth. It may be suitable for the doping of more types of impurities than what reported in this paper into Si and other semiconductors nanometer thin films, silylene and other two-dimensional materials and devices as well as ultra-shallow junction devices.

5 Conclusion

In this paper, we have experimentally demonstrated that some impurities, including Fe, Au, Al, Ga, Sn and In, can be doped into Si wafers with depths of tens nanometer but quite high concentrations by PDWOB at room temperature. Almost no etching effect occurs for the Si wafers during PDWOB. The physical mechanism of the PDWOB is room-temperature diffusion of impurities in Si assisted by vacancies and Si self-interstitials induced by plasma. The PDWOB is a powerful method for doping impurities into ultra-thin films and ultra-shallow junction devices of not only silicon but also other semiconductors. The PDWOB may also be applied to dope two-dimensional materials and devices due to its ultra-shallow doping depth, high surface concentration and very little etching effect.

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