Selective Double Diffusion of Zn and Si into GaAs Using Sputtered Si Masks

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Silicon diffusion into GaAs from a sputtered silicon film under an excess pressure of arsenic is described. The importance of the presence of arsenic for successful silicon diffusion is shown. The activation energy and diffusion coefficient have been obtained using a newly developed relationship between the diffusion depth and the diffusion coefficient. An approximate solution to the Si pair diffusion equation has been derived which gives excellent results. Self-aligned pn double-diffusion has been demonstrated by sequentially diffusing silicon and zinc.

1) INTRODUCTION

Impurity diffusion of dopants into III-V compounds has been recognized as a key technology in the fabrication of optoelectronic devices, such as laser diodes, photodetectors, modulators and optoelectronic integrated circuits (OEICs). Recently, much attention has been focused on the impurity-induced disordering (IID) of GaAs/AlGaAs multi-quantum well (MQW) structures for the fabrication of low threshold lasers. For example, very low threshold buried hetero-structure lasers have been demonstrated by selective diffusion of Zn [1] [2], or Si [3] [4] to disorder the MQW layers adjacent to the active region. It has been reported that a Si film acts as a good diffusion mask for Zn at low temperatures [5] [6], and that Si diffuses from the film at higher temperatures when the film is covered with SiO_2 [7], or is doped with As [8]. In this paper we report controlled Si diffusion into GaAs from a sputtered film of Si and the selective, parallel diffusion of Si and Zn to form a self-aligned lateral pn junction by double-diffusion. An approximate closed-form expression for the Si diffusion profile is given. Polynomial functions are derived by applying a least-squares method to a numerical solution of the equation for the Si pair diffusion [7].

2) EXPERIMENT

Standard (100) Cr-doped semi-insulating GaAs wafers were used as substrates. After degreasing the wafers, the surface was slightly etched with a solution of $NH_4OH:H_2O_2:H_2O$ (1:1:2). Then a Si film was deposited in an rf (13.56 MHz) magnetron sputtering system at room temperature with a target of undoped poly-Si. The background pressure of the vacuum chamber was about 1×10^{-6} torr. During the deposition the Ar pressure was 7×10^{-3} torr. The growth rate of the film was approximately 240 Å/min. The sputtered film was photolithographically patterned and etched in a $CF_4 + O_2$ plasma to provide silicon stripes for the selective diffusion. Several of the samples were then covered with a sputtered SiO_2 film in order to examine the effects of the presence of a cap film and its thickness dependence.

The Si diffusion was carried out in a closed quartz ampule at a temperature range from 850°C to 950°C. The volume of the ampule was about 9.5cc. To provide the excess arsenic pressure various amounts of elemental arsenic were loaded into the tube ranging 0 to 20 mg. To perform the double-diffusion the sample was then loaded into a new ampule for Zn diffusion at 650°C with elemental Zn and arsenic as diffusion sources. The diffusion depth was revealed by staining a cleaved cross section with $HF:H_2O_2:H_2O$ (1:1:10) under light illumination and measured with an optical microscope. Several samples were analyzed with secondary ion mass spectroscopy (SIMS) to measure the profiles of the diffused Si. Sputtered Auger electron microprobe was used to determine the As profile in the Si film before and after the Si diffusion process.

3) RESULTS AND DISCUSSION

The open circles in Fig. 1 show the SIMS profile of the diffused Si after 4 hours diffusion at 850°C. The concentration of Si at the surface is about 9×10^{20} cm^{-3} and
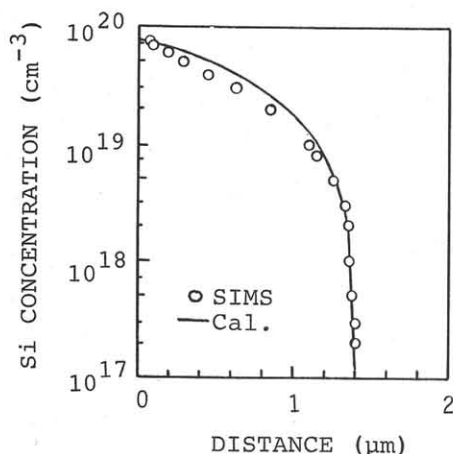
Fig.1. Calculated Si profile fitted to the SIMS data.

the concentration gradually decreases to 3×10^{18} cm^{-3}, where it drops quite rapidly. This behavior of the Si profile is similar to that of an SiO$_2$-capped or As-doped film [7] [8]. The solid line in the figure is the calculated result using the Si-Si pair diffusion model [7]. In the calculation the value of 4.68×10^{19} estimated by Greiner et al [7] was used for the thermal equilibrium constant of Si-Si pair formation. The curve fitting procedure has given the value of 5.0×20^{-13} cm^2/sec for the Si pair diffusion constant at 850°C which is quite consistent with previously reported values [7] [8]. This may suggest that pair diffusion is dominant in Si diffusion from the film under As pressure.

Figure 2 illustrates the strong influence of As in the diffusion of Si. These diffusions occurred at 850°C for 16 hours and show that without any As in the closed ampule no diffusion front was seen. As a small amount of As is added to the tube the diffusion depth quickly saturates to a uniform value. Figure 3 shows the sputtering Auger analysis of the Si film for the as-depositied case before diffusion (a), As-free (b) and As-rich (c) cases after diffusion. In the As-rich case drastic changes of the profile ocurred during diffusion and a concentration of 30% As was found in the Si layer. On the other hand, the profiles in the As-free case
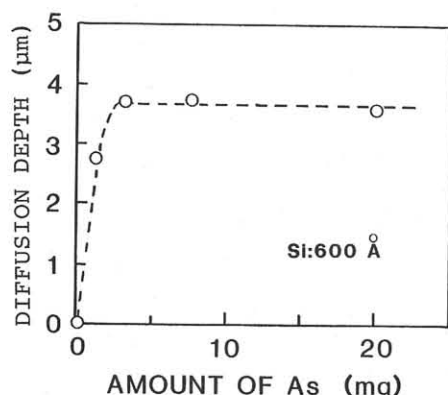
were almost unchanged from the as-deposited sample (a) as seen in the figure. From the comparison between As-free and As-rich cases, it can be concluded that the large amount of As in the Si film is diffused from the As atmosphere in the closed tube and not from the substrate. Furthermore, as the thickness of the Si film or the SiO$_2$ cap layer was increased (Fig. 4,5) the diffusion rate was seen to decrease. Additionally, Kavanagh et al [8] reported interdiffusion of Si at a hydrogenated amor- phous Si (α-Si:H) and GaAs interface when As is added to the α-Si:H film. An undoped α-Si:H film yielded a metallurgically stable interface. Thus one can speculate that As diffuses through the Si film during the thermal process and reaches the interface, creating an As rich region (or Ga vacancies), and that Si diffuses in association with these vacancies.

According to the Si pair diffusion model, the diffusion profile is determined by a Fickian diffusion equation with a concentration-dependent diffusion coefficient [7]. By
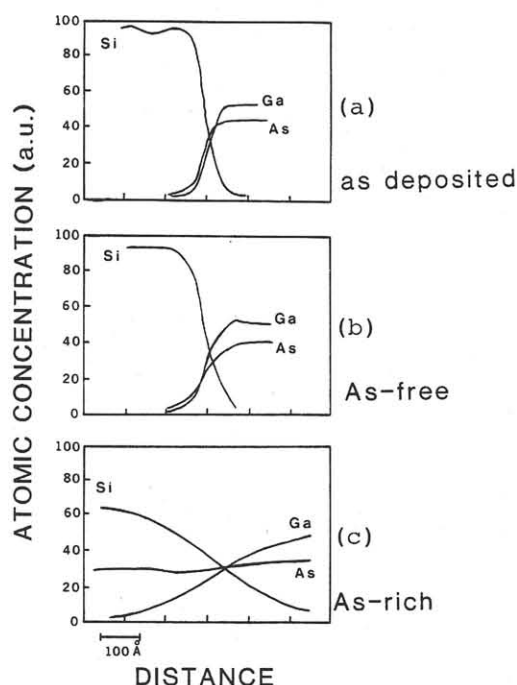

Fig.3. Auger electron spectra for (a) as-deposited and after 16-hr anneal at 850°C for (b) As-free, (c) As-rich case.

applying the Boltzmann transformation to the equation, $y = x/2(N_0/KD_{pair}t)^{1/2}$, where x is the distance from the surface, N_0 is the Si concentration at the surface, K is the thermal equilibrium constant for Si pair formation, D_{pair} is the diffusion constant of Si pairs and t is the diffusion time. A diffusion depth, d, is given by
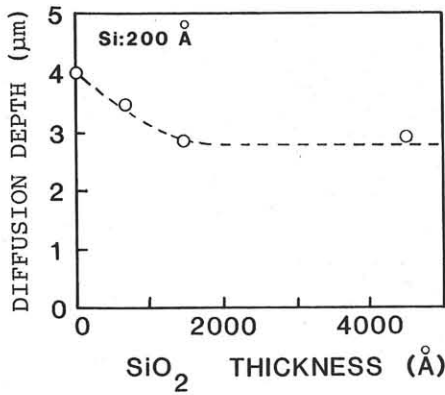
$$d = 2a_0(N_0/KD_{pair}t)^{1/2} \qquad (1)$$

Fig.2. Diffusion depth vs. As weight in ampule.

Fig.4. Effect of varying SiO$_2$ thickness on diffusion depth.
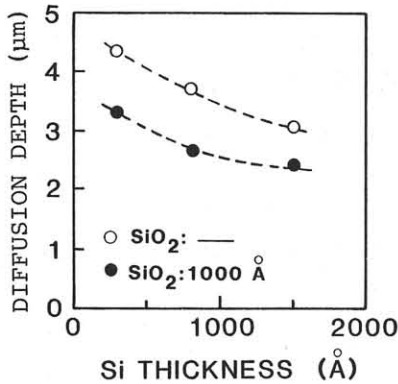
Fig.5. Diffusion depth vs. Si layer thickness for no SiO$_2$, and 1000 Å SiO$_2$.

$$C = 1 + C_1 y + C_2 y^2$$
$$C_1 = -0.990 - 0.685B + 0.0604B^2 \quad (2)$$
$$C_2 = -0.418 + 0.517B,$$

where B=N$_0$/K. The LSM was applied in the range of N$_0$/K from 0.6 to 2.8. If N$_0$ is about 1×10^{20} cm^{-3}, this range
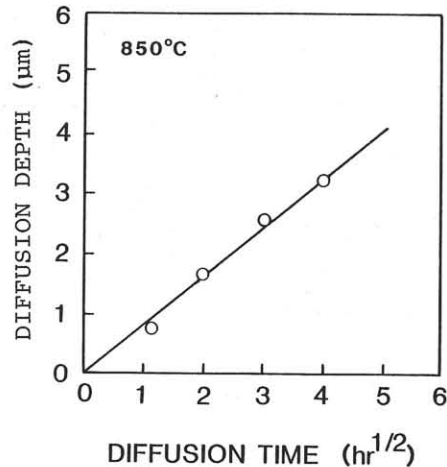

Fig.6. Relationship between diffusion depth and square root of diffusion time.

correspondes to the temperature range from about 800°C to 1200°C. The absolute error included in the approximation is 2×10^{-2} in the whole range and the relative error is less the 6% where C>0.01. A comparison of this approximation solution with both the numerical solution and with experimental data is given in Fig. 8.

The diffusion from the Si film and the selective Zn diffusion with a Si mask can be used for self-aligned, parallel n and p-type diffusion. Figure 9 is a set of the photographs of Zn, Si and "double" diffusion. The results of double
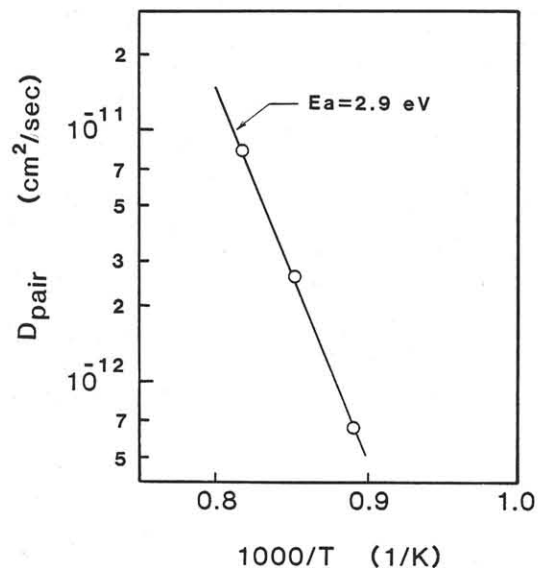

Fig.7. Diffusion coefficient of Si-Si pair plotter as a function of reciprocal temperature.

when the Si concentration becomes zero at y=a$_0$. The relationship between the diffusion depth and the square root of time is shown in Fig. 6. The diffusion was carried out at 850°C with 10 mg As in the tube, well beyond the saturation point for the diffusion depth vs. As weight. By changing the diffusion temperature with the amount of As held constant, the activation energy of D$_{pair}$ can be calculated. In the calculation, the surface concentration was assumed to be constant at 1×10^{20} cm^{-3} in this temperature range. As shown in Fig. 7 a straight line can be drawn through the data giving an activation energy of 2.9 eV. This is comparable to 2.6 ± 0.25 eV for Si diffusion from the As doped Si film [8].

The diffusion profile is given by solving the diffusion equation numerically. However, we have developed a useful closed-form expression to approximate the diffusion profile. Since the pair diffusion equation includes only the parameter N$_0$/K, polynomial functions can be derived in terms of y and N$_0$/K by applying a least-squares method (LSM) to a numerical solution of the diffusion equation. Thus the Si concentration, C, normalized to N$_0$, can be expressed as follows;

diffusion are depicted in Fig. 9 (a) where we sequentially diffused Si from the Si mask at 850°C, and then used the same Si layer as a mask for Zn diffusion at 650°C. This double diffusion technique may provide a self-aligned structure which is desired for numerous devices, such as IID buried heterostructure lasers.

A sputtered Si film has recently proven to be an excellent mask for wet-chemical etching of GaAs/AlGaAs system. The Si masks show comparatively small extent of undercutting and are usable in the highly selective etch, HF, which etches $Al_xGa_{1-x}As$ (x=0.4) 300 times faster than GaAs [9]. More detailed characteristics of the sputtered Si film as an etching mask appear elsewhere [10].
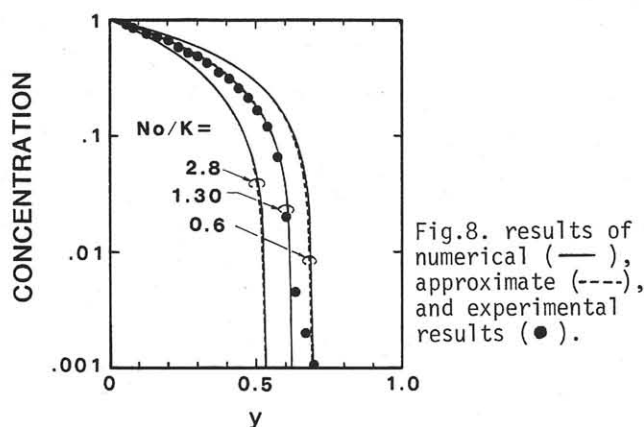

Fig.9. Set of photographs of Zn-, Si-, and double-diffusion.

Fig.8. results of numerical (——), approximate (----), and experimental results (●).

CONCLUSION

Controlled Si diffusion into GaAs from a sputtered Si film under an excess pressure of As has been developed. The importance of As at the interface has been emphasized. A useful closed-form expression for the diffusion of Si has been derived. The formation of a self-aligned pn junction by double diffusion has been demonstrated. The success of this study suggests a wide variety of applications of sputtered Si film in the processing technique for optoelectronic devices.

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