The Effect of Thermal Annealing on the Diffusion Profile of Nickel in GaAs Substrates

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Abstract

Diffusion of nickel in GaAs has been studied at 950ºC. The diffusion was enhanced during limited interval and for different quantities of As. Nickel atoms had diffused in the beginning due to the interstitial movement of atoms but large number of nickel atoms occupies substantial locations in p-type GaAs lattice. Measurements performed to the samples have showed good agreement between the nickel atoms concentration and majority charge-carriers in p-type semiconductor (holes). Measurements explained that electrical conductivity of p-type samples was not due to system heating but to the diffusion of nickel atoms occupying sites of gallium atoms.

Keywords: Ni/GaAs; thermal annealing; diffusion

تأثير التلدين الحراري على انتشار النيكل في قواعد الكاليوم ارسنايد

الخلاصة

في هذا البحث ، جرى دراسة أنماط انتشار النيكل في عينات من الكاليوم أرسنايد عند درجة حرارة تلدين 950ºC. جرى تحسين الانتشار من خلال إضافة مقادير مختلفة من الأرسنايد، إن ذرات النيكل تنتشر في بادئ الأمر بسبب الحركة البينية لها غير أن عدداً كبيراً منها يحتل مواقع استبدالية في الكاليوم أرسنايد المانح. أجريت القياسات الكهربائية للعينات وقد أوضحت تطابقاً جيداً ما بين تراكيز النيكل وتركيز الفجوات التي تعتبر حاملات الشحن الأغلبية في شبه الموصل القابل. أوضحت القياسات أن التوصيلية الكهربائية للعينات القابلة لم تكن بسبب تسخين المنظومة وإنما بسبب انتشار ذرات النيكل التي تحتل مواقع ذرات الكاليوم

Introduction

It was well established that elements in the first group of the periodic table change the electrical properties of compound semiconductors. Although, the descriptions of diffusion properties of these elements are limited especially for Ni-GaAs system. The diffusion of Ni in GaAs was first studied in 1972. It was found that diffusion profile does not submit to any standard mathematical relation, although the diffusion mechanism is not simple. Some results proved that diffusion mechanism is due to interstitial movement of nickel ions (Ni^+) and this process was assumed to take place near the sample surface, although sites of nickel atoms mostly found to be substitutional sites [1].

When nickel atoms are found with high concentration in GaAs, then they act like acceptor dopants. The dopant energy

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level for Ni-GaAs system is lying above the equivalence band by 0.11eV. A relation was given for estimation of diffusion coefficient (*D*) by fitting the results by the following relation [2]:

$$D = 1.4 \times 10^{-11} \exp\left(\frac{0.33eV}{KT}\right) \quad (cm^2/s)$$

$$....(1)$$

where *K* is Boltzman's constant and *T* is temperature

In this work, the diffusion of nickel in GaAs at 950°C has been studied and enhanced during limited interval and for different quantities of As considering fast, simple and reliable analysis. Such devices are common used in microelectronics, integrated circuits and low-scale semiconductors devices and photonics.

Experiment

Donor (n-type) GaAs slides were used with area of 1.1 cm^2, 0.2 mm thickness, crystal orientation of (100) and carrier concentration of $2x10^{16}$ cm^{-3}. The slides were first treated chemically in a 1% bromine solution in methanol and kept in quartz ampoule. The ampoule was evacuated to 10^{-4} mbar and then was sealed-off in 6 cm^3 volume. The ampoule was kept in an electronic-controlled oven with 950ºC to achieve diffusion. The diffusion range time was (30-240) minutes and samples were cleaned and arranged according to heated time.

Chemical etching was done for layers of the samples to recognize the diffusion profiles and test material properties. The removed thickness of material was calculated for sample using etching process technique.

The C-V measurements were performed to the samples using a mercury probe. Throughout C-V measurements, carrier concentration at the surface of sample was calculated. Chemical etching for layers of the slides and C-V and Hall effect measurements were repeated. Uniform doping of Ni in GaAs has been achieved. The Hall effect measurements were carried out considering to the following set of

equations [3]:

$$V_H = R_H J_x B_z W \quad (2a)$$

$$R_H = \frac{r_H}{qp} \qquad p \gg n$$

$$... (2b)$$

$$R_H = -\frac{r_H}{qp} \qquad n \gg p$$

$$....(2c)$$

Where(V_H)is Hall voltage, (R_H) is Hall coefficient, (J_x) is the current density along x-axis,(B_z) is the magnetic field applied along the z-axis, (*W*) is the depletion region width,(r_H) is Hall factor,(*q*) is the electron charge unit, and(*p*) is the concentration of positive charge carriers (holes)

Results and Discussion

Profiles in figure (1) declare that surface concentration (C_0) is high but it decreases with the distance from the surface until the volume concentration (C_B) is almost fixed. There is some dip between two curves in figure (1) of diffusion profile. The obtained profile agrees with Ni-GaAs, Ni-InAs and Ni-InP systems [4-9]. Table (1) gives values of C_B and C_0 those were measured from the profiles and the experimental circumstances for every diffusion profile. Table (1) and figure (1) show that nickel amount added to the ampoule did not cause large difference between diffusion profiles obtained due to low nickel vapor pressure even at 800ºC. So, nickel amount added initially was not enough to generate high pressure inside the ampoule compared with amount needed to generate such high pressure.

Figure (2) explains variation of Ni concentration as the distance from surface does for several time intervals (30, 45, 60, 240) min. The stable value of surface concentration (C_0) almost shows that equilibrium in surface happened in early stage of diffusion process although volume concentration (C_B) increases with time to reach maximum of $4x10^{16}$ cm^{-3}.

Figure (3) shows the effect of adding arsenic (As) to the ampoule where it

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causes C_B and C_0 to decrease. Considering the results of experiments 6 and 7 in table (1), we note that they are same in value despite that arsenic (As) quantity added differs in two experiments by 4 times. This confirms that addition of arsenic (As) does not assist to decrease the dip in diffusion profile.

According to C-V measurements, all samples were p-type after diffusion in case of adding arsenic (As) to ampoule for one time. It is important to confirm that electrical conductivity from p-type for samples was not due to heat treatment joined with diffusion process but due to existence and diffusion of nickel atoms. It is established that GaAs has the ability to change its conductivity from n-type to p-type when be heated to high temperatures due to thermal conversion phenomena, so heat treatment was performed to n-type GaAs slides [9-10] in the same manner of Ni diffusion. The samples were converted to p-type. The concentration of carriers is lesser than that for Ni diffusion by approximately 2 times [10], which supports that donor (p-type) conductivity of samples was enhanced due to the existence of nickel.

Table (2) explains results of diffusion experiments performed on samples with and without added arsenic. The table shows the concentration and mobility of the carriers for these samples as well as the concentration of atoms and vacancies using C-V and Hall effect measurements.

The diffusion profiles in this research agree with that of previous works on Ni-GaAs system and similar to other profiles of Ni-InP, Au-InAs and Cr-GaAs systems. It is surely been proved, according to this research and other researches, that interstitial diffusion for doping atoms takes place in the beginning course of diffusion process. Besides, Ni atoms act as an acceptor (p-type) dopant in GaAs samples. Such electrical behavior is usually due to occupation of nickel atoms to the original sites of GaAs [11]. This type of doping is known as substitution doping because the occupation of nickel atoms to interstitial sites converts electrical conductivity to the donor type (n-type). It is hard to explain saturation in C_B value at 5×10^{16} cm^{-3} after one hour of diffusion time if it is considered as interstitial doping.

We did not specify which atomic site in GaAs lattice was occupied by a nickel atom, the most accepted opinion confirms that nickel is from I group of periodic table and acts as an acceptor dopant (p-type) when occupies sites of GaAs which is from III group [12]. But figure (3) does not agree with this opinion because increasing (As) amount in the ampoule during the diffusion leads to increase vacancies concentration in semiconductor (GaAs) [13]. If Ni atoms occupy Ga sites, then this leads to increase the solid solubility for(Ni) in GaAs and figure (3) shows the inverse case. So the occupation of Ni atoms to As sites does not seem right.

Conclusions

Experiments showed that diffusion of Ni in GaAs have changed the conductivity of semiconductor to the opposite type. This could be explained due to(Ni) behavior as an acceptor donor. Analyzing diffusion profiles obtained in this work, it is clear that Ni atoms occupy original sites in GaAs lattice since the doping is substitutional, despite the fact that the diffusion process begins at interstitial sites initially. Annealing at 950ºC, experiments established that the occupation of Ga sites atoms is the most acceptable interpretation for the electrical behavior of Ni-doped GaAs.

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Table (1) values of C_B and C_0 measured from the profiles and the experimental circumstances for every diffusion profile

C_B x10^{16} (cm^{-3})	C_0 x10^{17} (cm^{-3})	Diffusion time (min)	As weight (mg)	Ni weight (mg)	Experiment No.
1.6	2.5	30	0	0.12	1
4	3.5	60	0	0.085	2
2.7	2.5	45	0	0.11	3
4	3	60	0	0.95	4
4	2.3	60	0	0.2	5
2.3	1.2	60	0.7	0.125	6
2.4	1.5	60	2.9	0.115	7
4	4	240	0	0.155	8

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Table (2) results of diffusion experiments performed on GaAs samples with and without added As

Ni diffused concentration + As	Ni diffused concentration	Quantities
2.7×10^{16}	3.7×10^{16}	Atoms concentration (cm^{-3})
1.5×10^{16}	2.4×10^{16}	Carrier concentration (Hall effect) (cm^{-3})
4.5×10^{16}	6.3×10^{16}	Carrier concentration (C-V) (cm^{-3})
542	412	Vacancies mobility ($cm^2/V.s$)
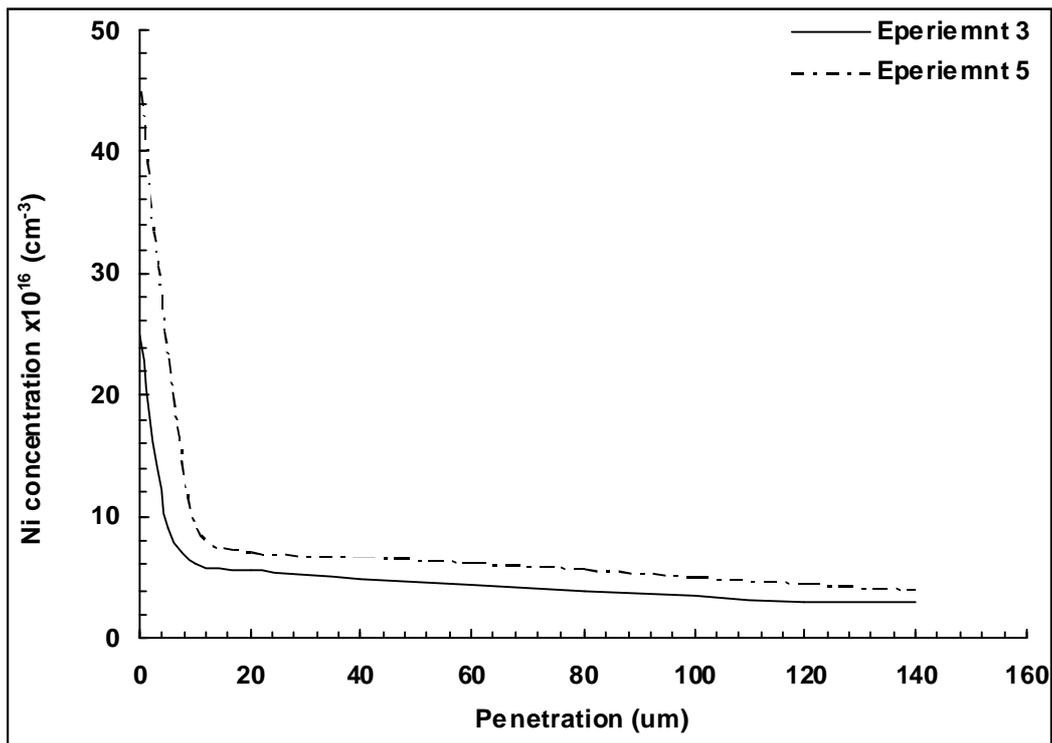
Figure (1) Variation of surface concentration of nickel *vs.* distance from surface

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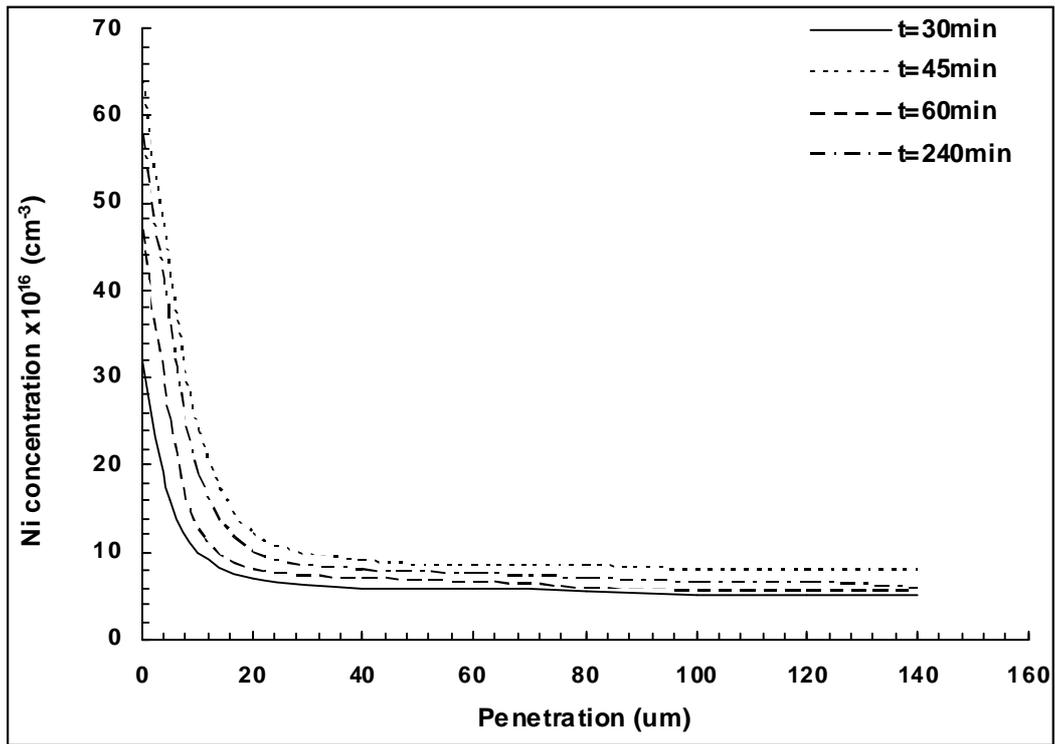
Figure (2) Variation of surface concentration of nickel *vs.* penetration for different diffusion time
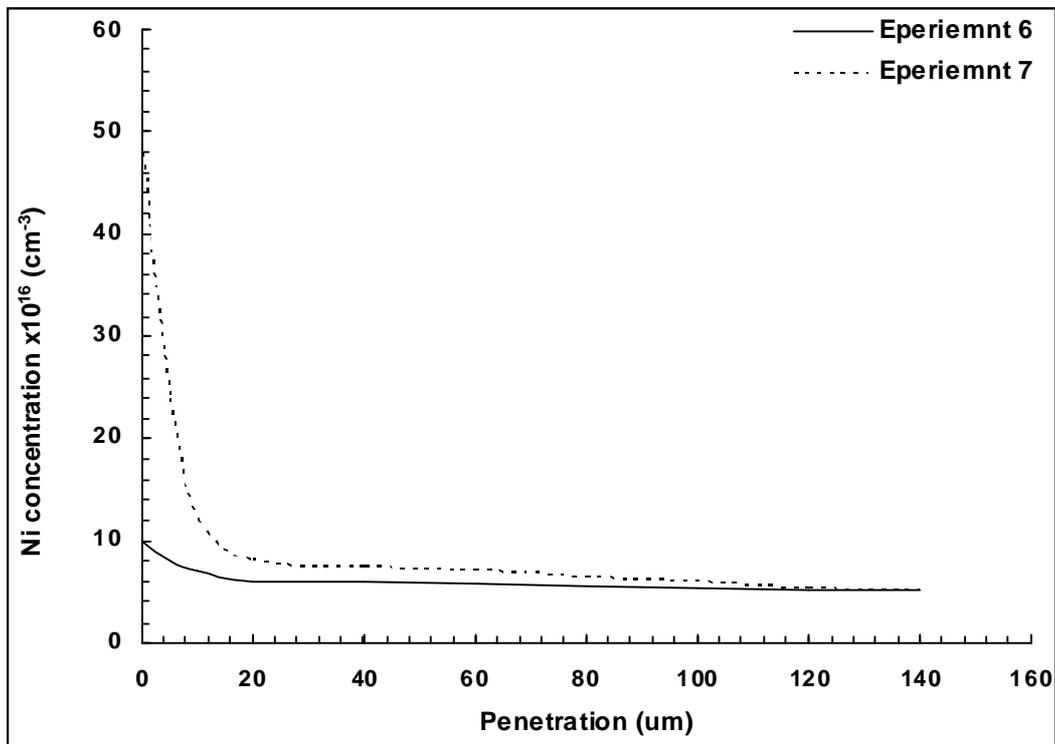
Figure (3) As-added variation of surface concentration of nickel *vs.* penetration for different diffusion time

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