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ELECTROPHYSICAL NATURE OF DEFECTS IN SILICON CAUSED BY IMPLANTED PLATINUM ATOMS

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The article of this study focuses on the defects caused by the platinum (Pt) atoms implanted in the silicon (Si) with the changes of their electrophysical properties after the high temperature thermal treatments. The introduction of the platinum atom into the silicon crystal lattice creates deep-level defect centers where the sensitive electrical properties and phenomena caused by temperature changes can be observed more clearly than in intrinsic defects. Of particular focus on platinum atoms incorporation, extensive studies have demonstrated significant changes of the defect structure in silicon and substantial transformation of its electrophysical properties related to the electrical conduction mechanisms and carrier scattering phenomena. Exclusive electrophysical effects were observed for platinum-doped silicon samples, which underwent high-temperature thermal annealing at 1050 °C and 1150 °C, primarily associated with the clustering of boron and platinum atoms, and the formation of complex defect aggregates. These thermal treatments enhance the interaction of isolated defects leading to the formation of clusters and complex defect entities, which greatly enhances the scattering mechanisms. These interactive effects of defects were found to be dominant in changing charge carrier transport and recombination processes in silicon crystals. Furthermore, experimental results showed a combination of scattering mechanisms that includes neutral defects, deep energy levels induced by platinum impurities, and their respective charged states. Platinum-induced defects thus enable multiple scattering mechanisms, and such hybrid mechanisms play a critical role in a silicon electrical and electronic behaviors, which influence the semiconductor applicability of the materials in high-temperature or high-performance, etc.
Keywords: *Charge carrier mobility; Conductivity; Thermal treatment; Temperature coefficient; Acceptor impurities; van der Pauw method; Vacancies; Crystallography*
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INTRODUCTION

In semiconductor technology, the thermal treatment at a high temperature and the metal-diffusion into silicon are important for changing the electrophysical characteristics of the material. They have a great influence over silicon crystallographic structure, charge carriers' concentration and mobility, and recombination processes. They are also chosen to improve the reliability of silicon-based microelectronic devices, provide a controlled spatial distribution of charge carriers, and enhance the thermal stability of the material. Among semiconductors, silicon (Si) is the dominant material, as it is cheap, mechanically strong, and can be synthesized in a sufficiently pure state to form high-quality monocrystals. An acceptor energy level is located near the top of a valence band [1] when an acceptor atom (B, Ga, or Al in the case of silicon) is located in the silicon crystal. These acceptor levels promote carrier generation (holes), thus helping to form p-type semiconductors. As a result, adjusting distribution and ionization energy of acceptor atoms in silicon is extremely important in microelectronics.

Also, when heavy metals like platinum (Pt), gold (Au), iron (Fe) and nickel (Ni) are incorporated in silicon, deep energy levels and defects form in this material [2]. These metals can introduce deep trap centers in the energy spectrum of silicon, which can have a profound impact on the mobility of charge carriers and mechanisms for conductivity. In particular, platinum atoms introduce deep energy levels in the band structure of silicon, thereby speeding up the recombination processes of charge carriers [3-5] In addition, at high-temperature processing, platinum atoms penetrate into the silicon lattice and occupy vacancies and interstitial defects [6]. Moreover, metallic atoms present in silicon act as electron and hole traps, which can either diminish their mobility, or, conversely, enhance their bulk conductivity. Those semiconductor processes are used in the production of silicon-based integrated circuits (ICs), high-speed transistors and sensor devices. Therefore, knowing the effect of the acceptor and/or metal atoms used to dope the silicon and studying their energy levels are paramount for accurate tuning of the electromagnetic properties of this material. This article presents the analysis of electrophysical changes arising from p-type silicon dopant by Pt atoms and high-temperature thermal processing conducted in this respect.

MATERIALS AND METHODS

Samples measuring 1×10×10 mm³, prepared from monocrystalline silicon with a resistivity of 5 Ω·cm and p-type conductivity, were used as the initial material [7]. Doping of silicon with platinum atoms was performed by gas-phase diffusion at temperatures of 950°C, 1050°C, and 1150°C for 5 hours in quartz ampoules evacuated to a vacuum of approximately 10^{-4} Torr. Afterward, the samples underwent a gradual cooling process to determine the resistivity,

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concentration and the mobility of the majority charge carriers in the grown films, the Van der Pauw method was used on a *HMS-7000* Hall effect measurement unit.

RESULTS AND DISCUSSION

It is known that in semiconductors, the temperature dependence of the mobility of charge carriers is given by the following expression:

$$\mu \sim T^m \cdot e^{-\frac{E_a}{kT}}.$$

Here, μ is the charge carriers' mobility, T is the absolute temperature, E_a is the activation energy, and k is the Boltzmann constant. In many cases, to achieve a linear relationship from equation (1), it is necessary to take the logarithm of both sides of the equation. Additionally, the mobility μ of charge carriers in monocrystalline silicon decreases with increasing temperature, exhibiting an inverse relationship [8]:

$$\mu \sim T^m.$$

Here, m is the temperature coefficient.

Charge carrier mobility in common p-type silicon samples doped with boron (p-Si<B>) normally retains such temperature dependence: informal of low temperatures (T < 150 K), it shows a weak or medium increase due to neighboring ionized impurities [9] scattering, whereas in the case of high temperatures (T > 150 K) - a highly mobility drops as a consequence of phonon [10] scattering. Which mechanism dominates depends on the doping concentration of the silicon where impurity atoms are incorporated, and the crystalline quality of the sample [11]. For instance, in the case of p-Si<B> samples, we noticed a temperature dependent charge carrier mobility in the range of 200–300 K with a temperature coefficient m = 0.4 (illustrated in the Figure 1). This implies that, beyond the acoustic phonon scattering at high temperature observed in the curve, further scattering mechanisms associated with structural imperfections (defects, clusters, dislocation points etc.) are being activated in samples treated by 5 h at 950 °C [12].

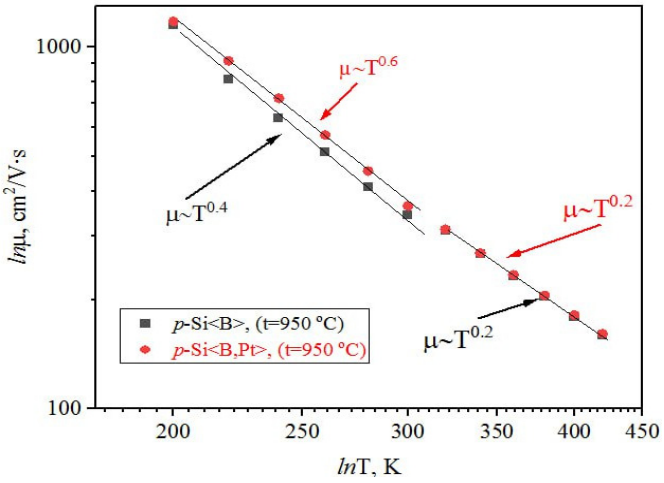

Figure 1. Logarithmic dependence of charge carrier mobility μ on temperature in p-Si<B> samples subjected to thermal treatment at 950°C and doped with Pt atoms.

Regarding the 200–300 K region, the temperature coefficient of charge carrier mobility rises from m = 0.4 to m = 0.6 in the sample of p-Si<B> when Pt atoms are diffusing in the substrate at high temperature of 950°C for 5 hours (see figure). This indicates that the Pt atoms, diffused into the silicon crystal lattice as a result of high-temperature processing, generate more complex structural damage and deep-level trap centers in silicon crystal, resulting in enhanced and temperature-dependent scattering mechanisms.

Between 300–450 K, the mobility of the charge carriers in p-Si<B> samples showed temperature dependence with a coefficient of m = 0.2 (figure shown). A quick recap of the underlying physical mechanisms behind this behavior is in order. Silicon possesses a moderate temperature regime at 300–450 K, as phonon scattering to charge carrier mobility prevails in this temperature range. We suspect scattering due to neutral defects or neutral impurity atoms in this case is more important due to the relatively low mobility coefficient m = 0.2 [13] Furthermore, because the boron atom concentration of the samples is very high (N_A>1018÷1019cm-3), this may also cause similar behaviors as reducing carrier mobility in heavily doped samples depends primarily on the scattering at impurity atoms and structural defects [14]. Finally, the presence of dislocations or other structural imperfections can also give rise to this reduction in temperature coefficient of mobility (e.g. (m = 0.2). It is more likely that this happens in the 300–450 K range where, in general, the interaction between charge carriers and defect structures is weakly temperature dependent.

A similar temperature dependence (μ~T0. 2) was also detected for p-Si<B,Pt> samples at the temperature range from 300 to 450 K (Figure 1). It is well known that in the case of p-Si<B> samples, the incorporation of transition metal

atoms such as Pt produces energy levels deep in the bandgap treated as deep-level impurities. These levels are related to defects that may be present in both neutral and positively charged forms [15]. These defects often exhibit neutral scattering center-like behavior – especially when related to Pt atoms – resulting in a weak temperature dependence of mobility. Moreover, Pt atoms serve as deep-level traps in the energy spectrum of the silicon crystal, being almost unchanged in a neutral state at high temperature due to the difficulty of entering a charged state [16]. As these defects stay in place in the neutral state during the temperature increases, they will serve as a scattering mechanism that is mostly independent of the temperature producing low value of mobility coefficient (m = 0.1÷0.3).

In addition, as can be found in the literature, low temperature coefficients, like the ones discussed here, are often how those of Si doped with Pt and other transition metals, such as Fe, Au, and Ni, are reported. The underlying cause of this behavior can mainly be ascribed to the generation of deep-level defects in silicon crystals by Pt atoms in turn activated by neutral scattering mechanisms. Thus, the equal temperature coefficient found in p-Si<B> and p-Si<B,Pt> samples (m = 0.2), proves that the dominant factor which causes scattering in this temperature range is neutral defect scattering. As we know, prolonged high-temperature thermal treatment leads to the redistribution of boron (B) and oxygen (O) atoms in the silicon lattice structure, resulting in the formation of small clusters or complexes. Therefore, as the concentration of intrinsic defects increases, so does the concentration of various intrinsic defects like vacancies, dislocations, and complex defect structures (e.g., double defects, clustered defects). Here in our case for p-Si<B> samples subjected to thermal treatment at 1050°C for 5 hours, we have seen the temperature dependence of charge carrier mobility in the full 200–450 K range with a temperature coefficient of m = 2.6 (Fig. 2). Such a large value cannot be accounted for by typical scattering mechanisms such as phonon or ionized impurity scattering. Instead, it suggests, at these high temperatures, boron atoms and other defects aggregate together to build complex defect centers, their effect in scattering not only remains high at high temperatures but may actually amplify [17]. Similarly, the addition of Pt atoms onto p-Si<B> samples at 1050°C for 5 hours led to a mobility coefficient of m = 2.3 in the 200–300 K range and m = 2.5 in the 300–450 K range. Traditional scattering mechanisms alone cannot explain these large values. They are rather rationalized by strong scattering from deep-level defects (trap centers) and cluster defects, and by related localized strain fields created by Pt inclusion. The defects provide ever stronger scattering centers for charge carriers at elevated temperatures.

For p-Si<B> samples heat-treated at 1150°C for 5 hours temperature-dependent mobility of charge carriers exhibited coefficients of m = 0.55 and m = 0.56 in the temperature ranges of 200–300 K and 300–450 K respectively (see Figure 3). These values (m=0.55÷0.6) are characteristic of a mixed scattering mechanism that arises from the joint contribution of acoustic phonon scattering (for which m ≈ 1.5) and neutral defect scattering (for which m ≈ 0.1÷0.3) [18]. This means that boron atoms and thus intrinsic defects in the silicon lattice redistribute due to the long-term high-temperature treatment, forming complex defects and clusters liable to exist both in neutral and charged states. This leads to temperature dependence of mobility that is significant, but smaller than what is commonly related to phonon scattering only.

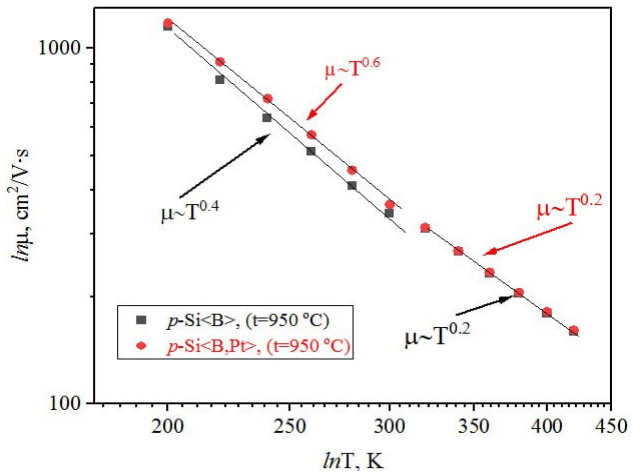

Figure 2. Logarithmic dependence of charge carrier mobility (μ) on temperature in p-Si<B> samples subjected to thermal treatment at 1050°C and doped with Pt atoms.

The charge carrier mobility in p-Si<B> samples with Pt atom doping at 1150°C for 5 hours showed a m = 0.6 temperature dependence in the 200–450 K range. It is well known that Pt atoms can create deep-level energy states in silicon, which create defect centers with neutral and charged states. The influence of such defects provides mostly larger temperature coefficients (m ≈ 0.5÷0.7) as compared to the scattering with the only neutral defects. This is because, in this case, the carrier mobility is determined not only by the neutral defects but also by the charged states of deep-level defects and trap centers. Hence, the intermediate value of m = 0.6 seen here, across the 200–450 K mid-range, signifies a combination of scattering mechanisms. Scattering is dominated instead by the joint action of neutral defects, deep-level energy states, and their ensuing localized strain fields in this regime. These defect centers are generally more thermally active at higher temperatures, thus perturbating more of the mobility of the charge carriers. Leading to a moderately strong temperature dependence of the mobility, typical of such a mixed scattering mechanism.

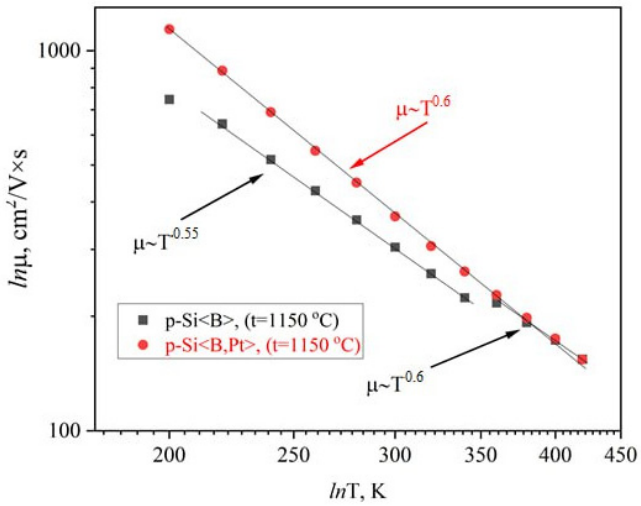

Figure 3. Logarithmic dependence of charge carrier mobility (μ) on temperature in p-Si<B> samples subjected to thermal treatment at 1150°C and doped with Pt atoms.

CONCLUSIONS

The following conclusions were established by the result of electrophysical changes observed in p-type silicon as a result of platinum (Pt) atom incorporation and subsequent high-temperature thermal treatments.

- Estimate of p-Si<B> samples collected from 200-300 K, which showed that the temperature coefficient of charge carrier mobility in p-Si<B> samples increased from m = 0.4 (before incorporation of Pt) to m = 0.6 (after Pt doping). This increase is maintained by the fact that Pt atoms in the silicon crystal forms deeper and more temperature-sensitive defect centers.

- The temperature coefficient (m = 0.2) for the p-Si<B> and Pt-doped p-Si<B,Pt> samples was obtained in the 300-450 K temperature range. This tendency is attributed to the superiority of scatterings of high concentration of boron and neutral crystalline defects.

- at the 1050°C, 5 hours thermal treatment, the value of the temperature coefficient reached the m=2.6 for the p-Si<B> samples showing the additional potential for propagation strong scattering mechanisms. These are mainly ascribed to boron atoms clustering and complex defect structures formation at high temperatures.

- In p-Si<B> samples doped with Pt atoms and annealed at 1150 °C, the mobility temperature coefficient in the range of 200–450 K is found equal to m = 0.60. This is ascribed to a combination scattering mechanism by neutral defects, deep-level energy states created by the Pt atoms, and their charged configurations.

Conflict of Interests

The authors declare that they have no conflict of interests

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ЕЛЕКТРОФІЗИЧНА ПРИРОДА ДЕФЕКТІВ У КРЕМНІЇ, СПРИЧИНЕНИХ ІМПЛАНТОВАНИМИ АТОМАМИ ПЛАТИНИ

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У статті цього дослідження розглядаються дефекти, спричинені атомами платини (Pt), імплантованими в кремній (Si), зі змінами їх електрофізичних властивостей після високотемпературної термічної обробки. Введення атома платини в кристалічну решітку кремнію створює глибокі центри дефектів, де чутливі електричні властивості та явища, спричинені змінами температури, можна спостерігати чіткіше, ніж у власних дефектах. Зосереджуючись на включенні атомів платини, масштабні дослідження продемонстрували значні зміни дефектної структури кремнію та суттєву трансформацію його електрофізичних властивостей, пов'язаних з механізмами електропровідності та явищами розсіювання носіїв заряду. Ексклюзивні електрофізичні ефекти спостерігалися для зразків кремнію, легованого платиною, які пройшли високотемпературний термічний відпал при 1050°C та 1150°C, головним чином пов'язані з кластеризацією атомів бору та платини, а також утворенням складних агрегатів дефектів. Ці термічні обробки посилюють взаємодію ізольованих дефектів, що призводить до утворення кластерів та складних дефектних утворень, що значно посилює механізми розсіювання. Було виявлено, що ці інтерактивні ефекти дефектів домінують у зміні процесів переносу носіїв заряду та рекомбінації в кристалах кремнію. Крім того, експериментальні результати показали комбінацію механізмів розсіювання, яка включає нейтральні дефекти, глибокі енергетичні рівні, індуковані домішками платини, та їх відповідні заряджені стани. Таким чином, дефекти, індуковані платиною, дозволяють реалізувати множинні механізми розсіювання, і такі гібридні механізми відіграють вирішальну роль в електричній та електронній поведінці кремнію, що впливає на напівпровідникову застосовність матеріалів у високотемпературних або високопродуктивних умовах тощо.

Ключові слова: *рухливість носіїв заряду; провідність; термічна обробка; температурний коефіцієнт; акцепторні домішки; метод Ван-дер-Паува; вакансії; кристалографія*