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Point defect–dislocation loop behavior in Si with a $TiSi_2$ film

S.B. Herner *, V. Krishnamoorthy, K.S. Jones

Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA

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Abstract

The behavior of end-of-range dislocation loops have been used to study the flux of point defects in Si after the formation of a $TiSi_2$ film. Extrinsic dislocation loops were formed in Si which then had 30 nm of Ti deposited and annealed to form $TiSi_2$. Control samples with loops but without a $TiSi_2$ film were annealed concurrently without a $TiSi_2$ film to provide a comparison. The density of the interstitials bound by the loops was measured by plan view TEM. Enhanced loss of interstitials bound by the loops in the silicided samples indicate a vacancy supersaturation caused by the presence of the $TiSi_2$ film. By assuming a constant flux of vacancies from the $TiSi_2$/Si interface to the layer of dislocation loops, we measure $C_V D_V$ values, where C_V = concentration of vacancies and D_V = diffusivity of a vacancy. By using a literature estimate of $C_V^* D_V$, where C_V^* = equilibrium population of vacancies, we derive $C_V/C_V^* \sim 1.2$ for Si annealed with a $TiSi_2$ film, which is in substantial agreement with the value from a previous study.

1. Introduction

Titanium disilicide ($TiSi_2$) has become the ohmic contact of choice in integrated circuits because of its thermal stability, low resistivity, and ability to self-align [1]. The titanium silicidation reaction, which results in a self aligned ohmic contact of $TiSi_2$ film on Si, has been much studied in an attempt to limit the thermal budget of IC wafers. Research has focused on ways to achieve the low resistivity C54 phase of $TiSi_2$ with the lowest temperature anneal. The desire to limit the thermal budget is driven, amongst other things, by the need to minimize dopant diffusion, which is intimately linked to the population of point defects in Si [2]. However, the formation and anneal of $TiSi_2$ can substantially alter the point defect population. This report gives some insight as to how the formation of a $TiSi_2$ film and subsequent anneal affects the point defect population through the examination of an extrinsic dislocation loop layer that lies immediately below the $TiSi_2$/Si interface in the Si substrate.

End-of-range (EOR) dislocation loops exist in many devices because device regions are typically pre-amorphized before dopant implantation to limit channeling effects [3]. It has recently been demonstrated that these dislocation loops can be used as quantitative detectors of point defects arising from ion implantation and oxidation [4,5]. Several studies have been conducted on the effect of the silicidation of thin Ti films on dopant diffusion and dislocation loops in Si, with the goal of determining the effect of $TiSi_2$ films on the point defect population in Si [6–9]. However, results from these studies have been conflicting. For example, Honeycutt and Rozgonyi [6] estimate a $C_V/C_V^* \sim 10^7$, where C_V = the con-

* Corresponding author.

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centration of vacancies in Si (/cm^3) and C_V^* = the equilibrium population of vacancies (/cm^3), after annealing 250 nm of Ti for 5 min at 800°C, while our previous study [9] finds $C_V/C_V^* \sim 2$ after annealing 30 nm of Ti for 1 h at 840°C, forming $TiSi_2$ in both cases, with both studies using buried Sb layers as markers. In a separate study, Honeycutt, Ravi, and Rozgonyi [7] found a substantial reduction in EOR extrinsic dislocation loops in Si with a $TiSi_2$ annealed at 900°C for several minutes while Lur, Cheng, Chu, Wang, Lee, Wann, Chao, and Chen [8] found a lesser degree of enhanced loop dissolution, and that loop dissolution varied with distance from the interface and implanted dopant species used to amorphize the Si.

In this study, we examine the behavior of dislocation loops after the growth and anneal of a $TiSi_2$ film. We compare loop behavior in Si annealed with and without a thermally grown $TiSi_2$ film. By studying the net density of interstitials bound by the loops and not just loop density, we find that the degree of enhanced loop dissolution in samples with a $TiSi_2$ film can be explained by a supersaturation of vacancies, and that the values extracted for C_V/C_V^* from loop dissolution are in substantial agreement with our earlier study [9].

2. Experimental

A Czochralski grown p-type Si wafer ($\rho < 100$ Ω cm) was implanted with 140 keV Ge^+ ions to a dose of 5×10^{14} cm^{-2} in order to amorphize the Si. The beam current was kept below 1 μA/cm^2 to limit possible dose-rate effects. The wafer was annealed in flowing N_2 at 800°C for 1 h to recrystallize the amorphized region and form the EOR loops. This annealing time has been shown to return the population of point defects to equilibrium values after the transient caused by ion implantation [10]. The wafer was cleaned in TCA, methanol, acetone, DI water, buffered oxide etch (10:1), and DI water in that sequence, to remove organic debris and the native oxide. The wafer was diced into two halves, and one half was immediately loaded in an electron beam deposition chamber which was pumped down to a vacuum better than 5×10^{-6} Torr. Titanium of 99.9% purity was then evaporated to a thickness of 30 nm. Both halves were immediately placed in a furnace in flowing forming gas (97% N_2 + 3% H_2) and annealed at 700°C for 20 min to form the silicide on the half with Ti. The halves were subsequently diced and annealed in forming gas at 700 to 890°C for 1 to 4 h to get significant point defect diffusion to the loop layer from the $TiSi_2$/Si interface. Samples with loops but without Ti were annealed concurrently and used as control specimens.

Samples were examined in a JEOL 200CX transmission electron microscope (TEM) operating at 200 keV. Samples for plan view TEM (PTEM) were prepared by standard mechanical lapping and chemical etching methods after the $TiSi_2$ film was removed by dipping in dilute HF (25%) for several minutes. Cross-sectional TEM (XTEM) samples were prepared by lapping and ion milling. Quantitative analysis of the dislocation loops was performed using weak beam dark field (g_{220}) PTEM micrographs. All the loops were measured in a representative area of 1.28 μm^2 in each sample. Loop diameters were measured in increments of 2.5 nm from 5 nm upwards by measuring the longest axis on the loop. The total number of loops of each size was multiplied by the area of that size loop and added to get the total area per cm^2 bound by the loops. Previous experiments have shown the loops to lie on the {111} habit plane [11]. The net density of Si interstitials bound by the loops in each sample was calculated by multiplying the area bound by the loops by 1.6×10^{15}/cm^2, which is the net density of Si atoms lying in the dislocation loop. Errors in counting were estimated by counting samples many times and obtaining an average and standard deviation, as has been described in more detail in Ref. [11].

3. Results and discussion

Fig. 1 shows the typical microstructure of a sample with a silicide film. The distance from the $TiSi_2$/Si interface to the loops is approximately 120 nm and the interface is rough, which is typical for films annealed at this temperature. Electron diffraction and sputtering Auger electron spectroscopy analysis of the silicide showed that a TiO_xN_{1-x} layer formed on top of the C54 phase $TiSi_2$ layer (Fig. 2) [12]. This is due to Ti's strong affinity for

Fig. 1. Representative cross sectional TEM micrograph showing the bilayer film and loop layer. The sample was annealed for 1 h at 840°C.

gettering gases like oxygen and nitrogen [13]. Since it is also common to employ a TiN diffusion barrier on top of $TiSi_2$ ohmic contacts in actual devices, this structure is not entirely unrepresentative of actual devices [14]. Analysis of the annealed samples shows that the loops coarsen with increasing time and temperature (Fig. 3). A previous study has shown that growth of the loops is substantially complete after a 1 h 800°C recrystallizing anneal in an inert ambient [15]. Further annealing results in a coarsening of the loops. While the number of loops decreases, the increase in size of the remaining loops maintains the net number of interstitials bound by the loops to approximately the same value [15,16].

To calculate the effect of the $TiSi_2$ film on point defects, the net density of interstitials bound by the loops in the samples with a $TiSi_2$ film was subtracted from the net density of interstitials bound by the loops in the control samples (no $TiSi_2$ film). Fig. 4 shows that the loops in the silicided samples are losing interstitials at an enhanced rate at 840 and 890°C. Both sets of samples annealed at 700°C show the same amount of interstitials bound by the loops. We attribute this to the smaller value of vacancy diffusivity at 700°C, and therefore confine further discussion to the 840 and 890°C samples. While net shrinkage of the loops is small, it is consistent and becomes more obvious with longer annealing times. The increased loss of interstitials shows that the $TiSi_2$ film is enhancing the dissolution of the loops. Note that the loss of interstitials is greater in the 890°C samples than the 840°C samples. The four hour 890°C anneal result is attributed to measurement error. The trend of continuing enhanced dissolution in the samples with a $TiSi_2$ film is apparent.

We have previously established that the formation and anneal of a $TiSi_2$ film results in a vacancy supersaturation in the underlying Si [9]. By assuming that a flux of vacancies from the $TiSi_2$ film is completely captured and annihilated by the loops, we can integrate the flux over the distance, giving a $C_V D_V$ product by:

$$\int_0^d \Phi \, dx = C_V D_V \qquad (1)$$

where Φ = the flux of vacancies (vac/cm^{2}s) measured after each annealing time, d = the distance from the interface to the loop layer (cm), and D_V = the diffusivity of a vacancy (cm^2/s). The values for Φ are from Fig. 4. This assumes: (1) loop dissolution is due solely to loop–vacancy recombination, (2) enhanced dissolution of the loops due to the presence of the $TiSi_2$ film is constant with time, and (3) a small barrier to vacancy–loop combination, which has not been proven but is a reasonable assumption. While no numeric estimate has been made of the energy barrier to recombination of a 'free' vacancy and an extrinsic dislocation loop, previous studies of interstitial supersaturation growth of dislocation loops has shown strong evidence that 'free' interstitial–dislocation loop recombination is diffusion limited, and not reaction limited [10]. Given that 'free' vacancies have an opposite strain state to that of extrinsic dislocation loops, we believe it is

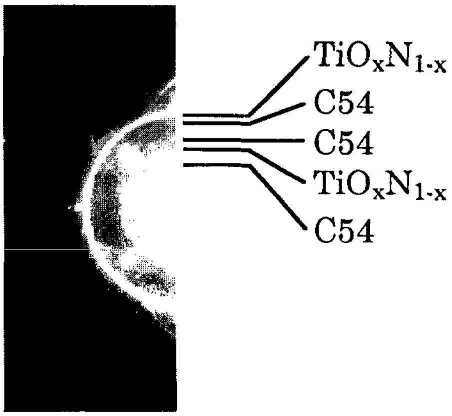

Fig. 2. Electron diffraction patterns of the films and Si substrate, showing the C54 $TiSi_2$ pattern and TiO_xN_{1-x} pattern. Note the double diffraction rings from the films.

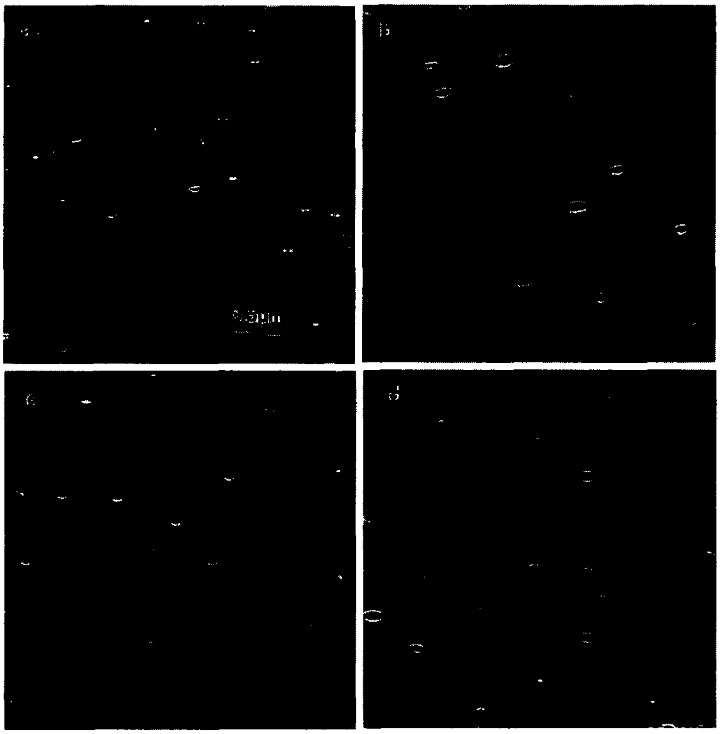

Fig. 3. Plan view TEM micrographs of samples annealed at 890°C: (a) and (b) without a film and (c) and (d) annealed with a $TiSi_2/TiO_xN_{1-x}$ film. Samples were annealed for (a) and (c) 1 h, and (b) and (d) 4 h.

reasonable to assume a that 'free' vacancy–dislocation loop recombination is similarly diffusion limited and not reaction limited. If there is a large barrier to this reaction, this method would result in undercounting the number of vacancies produced by the presence of the $TiSi_2$ film. Fig. 5 plots these $C_V D_V$ values. Since the 840°C one and two hour anneals did not show a loss of interstitials, those samples are not shown in Fig. 5. The greater dissolution of the loops in the 890°C annealed samples is explained by the larger D_V value.

By using a literature value for $C_V^* D_V$, we can

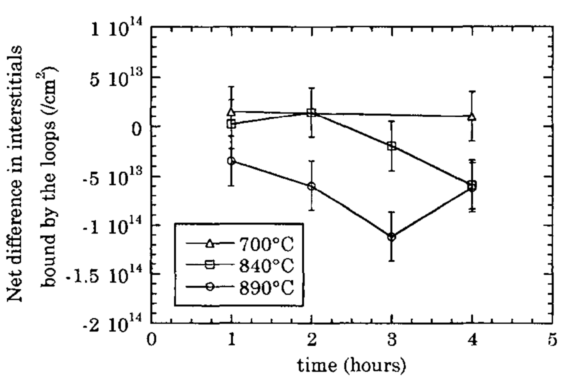

Fig. 4. Plot of the net difference in interstitials bound by the loops in the samples without a film and samples with a $TiSi_2$ film.

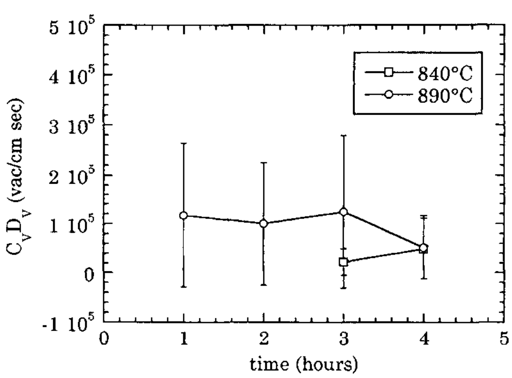

Fig. 5. $C_V D_V$ values for the samples arrived at by solving Eq. (1) for various times, using the data from Fig. 4.

now compare the results of our previous study [9], with this one. In our previous study, we measured $C_V/C_V^* \sim 1.4$ to 2 (depending on anneal temperature) by measuring the diffusion of Sb in thin delta doped layers, with same deposited Ti thickness (30 nm). We note that in the previous study [9], the samples received a single anneal, whereas in this study, the samples are first annealed at a lower temperature to form the silicide and then given a higher temperature anneal. Cross-sectional TEM showed the morphology of the films to be the same in both cases. After a one hour anneal at 890°C, our previous study measured a C_V/C_V^* of ~ 1.4 in Si with a $TiSi_2$ film. In this study, after one hour at 890°C, we have a $C_V D_V = 1.2 \times 10^5/\text{cm} \cdot \text{s}$. If we use the value of Tan and Gösele [17] for $C_V^* D_V$, which is $1.03 \times 10^5/\text{cm} \cdot \text{s}$ at 890°C, this results in a C_V/C_V^*, ~ 1.2 for this study, showing excellent agreement. There are several possible sources of error in the calculations: (1) the $C_V^* D_V$ value, which can vary by an order of magnitude, (2) the loop measurements, and (3) measuring diffusion in Czochralski grown Si versus the MBE grown Si used in the previous study, which can be different due to the presence of point defect traps [9,18].

This accelerated dislocation loop dissolution is in broad agreement with the results of earlier studies [7,8]. However, we did not observe complete elimination of the loops even after annealing at 940°C. These results agree with Lur, Cheng, Chu, Wang, Lee, Wann, Chao, and Chen [8], who did not eliminate EOR loops after 30 nm Ti deposition and annealing at 900°C for 1 h. The continued loss of interstitials from loops in the silicided samples at 890°C with time indicates that the non equilibrium point defect flux from the $TiSi_2/Si$ interface is at least partially continuous long after $TiSi_2$ growth is complete [19]. This indicates that the presence of the film and not just its growth alters the point defect population. A similar effect has been observed in Si_3N_4 films, in which chemical vapor deposition of the nitride films on Si cause a vacancy supersaturation and interstitial undersaturation [20,21].

4. Conclusion

Formation and annealing of a $TiSi_2$ film on Si that has a layer of extrinsic dislocation loops from previous ion implantation results in enhanced dissolution of the loops compared to Si without a $TiSi_2$ film. The continued enhanced dissolution of the loops with time at annealing temperatures indicates that the point defect perturbance at the $TiSi_2/Si$ interface is at least partially continuous with time. Comparison with previous work showing the presence of the film to cause a vacancy supersaturation indicates the enhanced loop dissolution can be accounted for by loop–vacancy recombination.

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