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TRANSMISSION ELECTRON MICROSCOPY AND ELECTRICAL PROPERTIES MEASUREMENTS OF LASER DOPED SILICON AND GaAs

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ABSTRACT

High quality silicon p-n junctions have been prepared by alloying a vacuum evaporated Al film into n-type Si and by epitaxial regrowth of an As doped Si amorphous layer onto p-type (100) Si by a single short pulse of ruby laser radiation. Transmission electron microscopy investigations indicated that a defect-free epitaxial layer was grown on the (100) Si surface; however, some polycrystalline structure in the very near-surface region was observed, which does not seem to affect the junction characteristics. Laser assisted junction formation in GaAs was demonstrated by alloying Mg films into n-type GaAs; however, diode characteristics show a large leakage current which may have been caused by the surface damage.

INTRODUCTION

The use of laser radiation to drive a surface-deposited dopant into Si and GaAs substrates to form p-n junctions has been investigated by a number of authors.[1-5] This technique is important because it is a much simpler and more easily automated process than thermal diffusion and ion implantation. This is particularly advantageous for devices such as solar cells which require high-volume, low-cost fabrication techniques to be economically competitive. With photovoltaic applications in mind, we have studied junctions formed by the deposition of B[4], Al, and As-doped Si onto Si and Mg onto GaAs, followed by irradiation with a Q-switched ruby laser. Our results indicate that a nearly ideal abrupt junction with low leakage current can be obtained in the Si system. Silicon solar cells fabricated by this technique have shown AM1 efficiencies as high as 10.6% without antireflection coatings.

EXPERIMENTAL METHODS

Polished 10 Ω-cm n- or p-type Si wafers and Si-doped n-type GaAs wafers were used as substrates. Thin film evaporations were performed by electron-beam vacuum-coating in a vacuum of 10^{-6} torr. Prior to evaporation, the silicon wafers were cleaned to remove organic and metal contaminants.[6] They were then immersed in a solution of HF:H_2O (1:10) and finally rinsed in distilled water. Ellipsometric measurements showed that the thickness of the SiO_2 layer

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after such treatment was ∼ 20 Å. Laser annealing was performed with a Q-switched ruby laser which delivered an ∼ 40 nsec pulse on a 5/8" diameter spot. Electrical measurements used included van der Pauw measurements to determine the electrical activity in the doped layer, and dark I-V and reverse-biased capacitance measurements to study the junction characteristics. The perfection of the doped layer was examined by transmission electron microscopy.

RESULTS AND DISCUSSION

I. Junction Formation in Silicon

A. Aluminum Alloyed Junctions

Aluminum was evaporated on Si at a deposition rate of 10 Å/sec to thicknesses of 50 to 250 Å. After laser treatment, the remaining Al was removed with HF:H_2O (1:1). Table I gives the electrical parameters of the alloyed layers. For Al films up to 100 Å thick, roughly 15% of the Al atoms were driven into substitutional sites by the laser treatment. Judged from the electrical activity, the substitutionality of Al in Si appears to saturate at a value of ∼ 10^{16} cm^{-2}. From previous work,[4] we know that the dopant concentration obtained by this technique can be well above the saturation solubility limit. That this was the case in the present studies was confirmed by subsequent annealing of the sample at 500°C for 30 min, which showed that the electrical carrier concentration was decreased by a factor of four. The hole mobility in all of the samples shown in Table I seems low and thicker films exhibited even lower mobilities.

Table I. Al deposited on Si

	ρ ($\Omega/\square$)	μ ($cm^2\ V^{-1}\ sec^{-1}$)	n (cm^{-2})
50 Å	96	13	5.0×10^{15}
100 Å	64	10	9.4×10^{15}
200 Å	75	9	9.4×10^{15}
250 Å	85	8	9.4×10^{15}

The results of measurements of the forward and reverse bias current in a small mesa diode ($A = 1.115 \times 10^{-3}$ cm^3) are shown in Fig. 1. The forward current follows the ideal-diode equation $I = I_0\ [\exp(eV/Akt)-1]$ with A = 1.20 over a reasonable range, which indicates that charge recombination and generation within the space charge region is quite low in comparison with that generally obtained for thermally-diffused junctions. The leakage current in the diode is also low as indicated from the low reverse-bias current. The reverse-bias capacitance plotted as C^{-2} vs V is shown in Fig. 2. The straight line indicates that the capacitance varied with voltage as $(V + V_{jct})^{-0.50}$ which shows that the dopant distribution in the

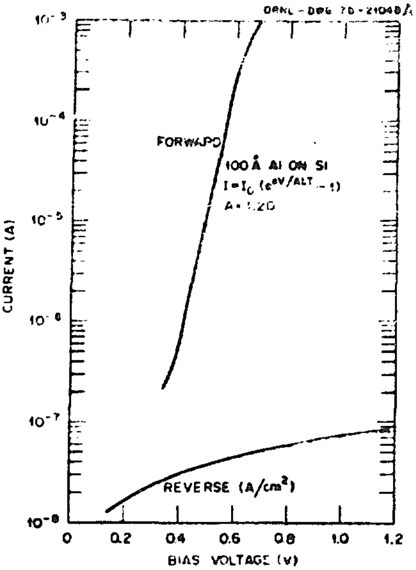


Fig. 1. I-V characteristics of laser treated Al alloyed junction.

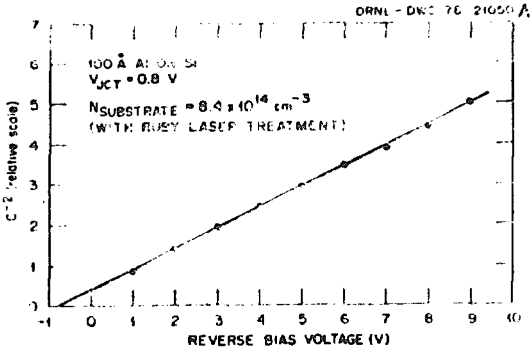


Fig. 2. Reverse biased C-V measurements of laser treated Al alloyed junction.

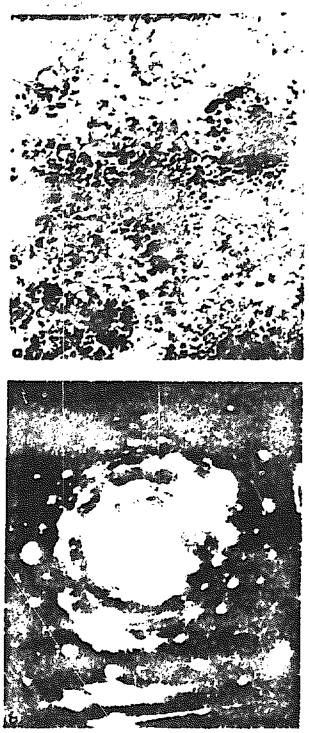
space charge region changes abruptly from p- to n-type. The dopant concentration measured in the depletion region is in good agreement with that obtained by Hall effect measurements.

Figure 3a is an electron micrograph of an 150 Å Al-deposited laser-treated specimen. The micrograph shows islands of aluminum oxide and silicon polycrystalline regions near the surface and this was confirmed by selected area diffraction patterns, as shown in Fig. 3b. The low mobility values in Table I may be due to these polycrystalline regions. Ellipsometric measurements on the sample surface indicated that more than one phase of an aluminum oxide layer existed on the surface. The index of refraction of the oxide film varied from 1.9 to 3.1 with thicknesses in the range of 300 to 500 Å.

Aluminum-deposited laser-annealed Si solar cells have been fabricated and tested under AM1 illumination. Without antireflection (AR) coatings and back surface fields, we typically obtain $V_{OC} \approx 555$ mv, $I_{SC} \approx 27$ ma/cm^2 and FF ≈ 71%, which results in a conversion efficiency of ≈ 10.6%. The aluminum oxide formed on the cell surface may serve as a partial AR coating but this has not yet been definitely established. Higher efficiency cells are anticipated by better control of the laser parameters.

B. Epitaxially Grown Junctions

It was demonstrated recently by Lau et al.[7] that a single pulse from a Q-switched Nd-YAG laser can recrystallize an amorphous Si layer deposited on a (100) Si substrate. Here we have used a similar technique to grow an epitaxial junction on (100) silicon. Czochralski-grown silicon, heavily doped (1×10^{19} cm^{-3}) with arsenic, was used as the deposition source. A 500 Å layer of amorphous silicon was evaporated onto a p-type substrate at a rate of 10 Å/sec. A single pulse from a ruby laser with energy density of 1.5 J/cm^2 was used to recrystallize the film. Figure 4a is a bright-field electron micrograph of the laser-treated, As-doped epitaxial layer. No defects, either in the form of clusters or extended defects such as dislocations or stacking faults, were observed within the microscope resolution of 10 Å. A diffraction pattern of a selected area from the same specimen is shown in Fig. 4b. It shows that the deposited layer has grown in the same orientation as the underlying substrate. The complete regularity in the diffraction pattern is also taken as evidence of the perfection of the lattice in the grown layer. The region at the interface between the deposited layer and the substrate was examined carefully, and no defects in any form were observed. The electrical activity of the epitaxial layer, as measured by the van der Pauw technique, gave $n = 3.3 \times 10^{14} cm^{-2}$, $\rho = 206\ \Omega/\square$ and $\mu = 91\ cm^2/V$ sec. Due to the higher vapor pressure of As relative to that of Si, a preferential As deposition will occur during evaporacion from the melt, which accounts for the high value of the free-carrier concentration. Dark I-V and reverse-biased C-V measurements on an epitaxial mesa diode are shown in Fig. 5 and Fig. 6, respectively. The near unit value of A, the small reverse bias current, and the straight line from the C^{-2} vs V plot give evidence that a superior abrupt junction has been formed.



[illegible]

[illegible] electron diffraction pattern.

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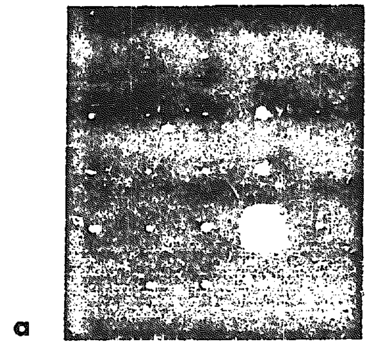

Fig. 4. Electron micrograph of laser treated As doped epitaxial layer.

a. Bright field electron micrograph.

b. (100) electron diffraction pattern.

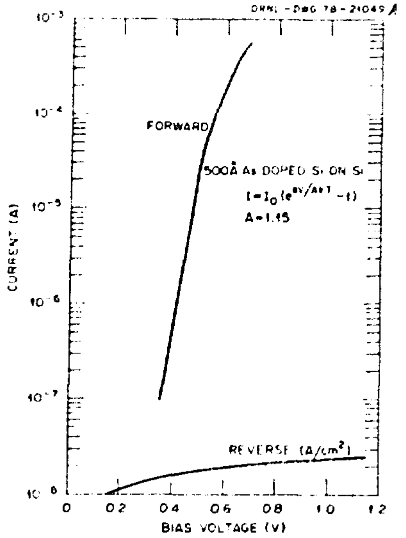

Fig. 5. I-V characteristics of laser treated As doped epitaxial junction.

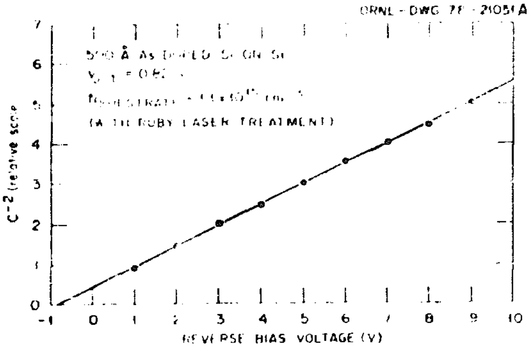

Fig. 6 Reverse biased C-V measurements of laser treated As doped epitaxial junction.

II. Junction Formation in GaAs

Some preliminary studies have been carried out on junction formation by deposition of 200 Å of Mg on (100) Si-doped GaAs containing an initial dopant concentration of 7 x 10^{17} cm^{-3}. The deposition rate was 15 Å/sec. Laser annealing was performed with pulses of three different energy densities, i.e., 0.3 J/cm^2, 0.8 J/cm^2, and 1.5 J/cm^2. After laser treatment,the Mg remaining on the GaAs surface was removed with hot H_2O:NaOH (10:1 by weight), followed by H_2O:CrO_3 (5:1 by weight). The low-energy laser radiation (0.3 J/cm^2)did not melt the Mg film, so an alloy did not form. High energy radiation (1.5 J/cm^2) leads to significant surface damage and vaporization of both the Mg and the GaAs substrate. Surface damage was greatly reduced when a laser energy density of 0.8 J/cm^2 was used. However, some microcraters were still observed by optical microscopy. The electrical activity of the Mg-deposited, laser-treated (0.8 J/cm^2) GaAs is given in Table II. For comparison, the data from 35 keV Mg-implanted, laser-annealed GaAs are also included. Comparable data were obtained for the carrier concentration and mobility. However, the Mg-deposited laser-treated p-n junction had a large leakage current, which may have been caused by microcraters on the surface. Due to the relatively large susceptibility of GaAs to surface damage, it may be that good alloyed junctions can be formed only within narrow ranges of laser parameters and film thicknesses.

Table II. Mg deposited on GaAs

	σ (Ω/□)	μ (cm^2 V^{-1} sec^{-1})	n (cm^{-2})
200 Å	45	29	4.7 x 10^{15}
Mg^+ implant (35 keV, 5x10^{15} cm^{-2})	64	24	4.1 x 10^{15}

CONCLUSIONS

High quality p-n junctions can be formed by the use of laser pulses to induce diffusion, alloying, and annealing of films deposited on silicon substrates. Due to the simplicity and low cost of this type of process, we anticipate that the methods discussed here, after further development, will be extremely useful in the high-volume fabrication of solar cells.

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