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Precise chemical analysis development for Si and GaAs surfaces

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Abstract

Precise Chemical Analysis (PCA) was developed to allow the study of non-interconnected atoms on crystalline semiconductor surfaces, such as those produced during Rapid Thermal Processing (RTP) of Silicon and electron beam lithography on GaAs. The PCA method is based on selectively dissolving the different components present on the semiconductor surface using preferential etchant solutions. After etching, the etchant solution, containing the etched component, is analysed by a photometric technique.

In this paper we present photometric measurements of the amount of “free” (non-interconnected) atoms which remain on semiconductor surfaces following electron beam and RTP processing. In this context, “free” atoms are those presenting in any form other than crystalline GaAs or Si, for instance, those in the form of surface oxides. Using the PCA method, free Ga and As were detected on GaAs surfaces after electron beam lithography. Free Silicon, Boron and Phosphorous atoms were found on silicon surfaces after RTP.

The concentration of boron diffused into a silicon wafer during RTP was also carried out by means of slight surface etching. We estimate the accuracy of this PCA method at 2% for Ga and 5% for all other elements.

Keywords: Precise Chemical Analysis, Rapid Thermal Diffusion, Silicon, Electron beam lithography, GaAs

1. Introduction

The fabrication of semiconductor devices requires several processes such as lithography, contact deposition and thermal treatments which affect the near-surface structure and composition of the semiconductor wafer. These process-induced changes can ultimately affect the device performance. It has been noted [1,2] that both structural and compositional changes at the surface are accompanied by thermomechanical strain which may lead to point defect motion or atom migration and dislocation generation within the crystal.

In this work, we present investigations of the changes in the surface composition caused by semiconductor processing of GaAs and Silicon wafers. In particular, we measure the concentration of free atoms, Ga and As in the case of GaAs and Si in the case of silicon, generated by semiconductor processing. In this context “free” atoms are those presenting in any form other than crystalline GaAs or Si, for instance, in the form of surface oxides.

We also apply the PCA technique to the determination of the amount of boron diffused into the silicon wafer during rapid thermal processing by slightly etching the surface and subsequently using the PCA method. Further investigations of the semiconductor surfaces were performed using optical microscopy and SEM.

2. Experimental Procedure

Precise Chemical Analysis of Gallium Arsenide

Epiready GaAs (100) substrate wafers, or wafers with an epitaxially grown *n*-type layer were used throughout this study. A number of pairs of samples, typically 5 x 5 mm² in size, were cleaved from both processed and unprocessed areas of the wafer. One sample from each pair

was processed and an identical unprocessed sample was put through the same photometric analysis to provide normalizing data.

The samples were initially cleaned in isopropanol and in HCl for 10 minutes. Each sample had its edges and back surface coated with protective lacquer so that only the front processed face was exposed to the photometric chemicals.

After electron beam irradiation, the GaAs sample was put into HCl immediately to reduce the time spent exposed to air. "Free" Ga and As were dissolved off the front surface of each sample by immersion for c.1 hour in typically 3 ml (enough to cover the sample surface) of 36% (12N) hydrochloric acid, followed by a rinse in distilled water. The rinse was collected and added to the HCl solution. In order to ensure all the "free" Ga and As had been etched off in the first HCl immersion, subsequent HCl immersions were undertaken and the resultant solutions photometrically analyzed to confirm that after the first HCl immersion, identical concentrations of "free" Ga and As were detected from both the processed and non-processed sample surfaces.

The concentration of Ga dissolved by the HCl was photometrically measured by forming a Ga-complex with xylenol orange ($C_{31}H_{32}N_2O_{13}S$) at a *pH* of 1.8. About 10 ml of water was added to 5-10 ml of the HCl solution, and the solution buffered to a *pH* of 1.8 (using ~ 1000 ml of CH_3COONa and HCl). About 2ml of a 0.1% xylenol orange solution was added to the HCl solution and made up to 25 ml with a buffered acetic acid solution. Twenty-five millilitres of a reference solution was also prepared by adding 2 ml of the xylenol orange solution to distilled water buffered to a *pH* of 1.8 with acetic acid.

The As concentration was determined photometrically using a blue arsenic-molybdenum complex, formed after initially oxidizing As(III) to As(V). Firstly, 0.2 ml of H_2O_2 was added to 5-10 ml of the HCl solution, and the mixture heated to decompose excess H_2O_2 . Then 1 ml of 1% ammonium molybdate solution (either $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ or $5(NH_4)_2O \cdot 12MoO_3 \cdot 7H_2O$) and 0.4 ml of either hydrazine or hydrazine salt (chloride or sulphate) were added and the mixture warmed for 15 min in a water bath. After cooling, the

mixture was made up to 25 ml with distilled water.

An FEK-56M photometer was used to measure absorbance, with a green (540 nm) filter and a 20-mm working distance used for the Ga determination, and a red (720 nm) filter and 50-mm working distance used for the As measurement. For both Ga and As, concentrations in the final solution over the range 0.1-1.0 $\mu\text{g/ml}$ were measurable, with an accuracy of about 2 % for Ga and about 5 % for As. The masses of free Ga and As from each processed sample were normalized to the unprocessed sample mass measurements in every case.

Precise Chemical Analysis of Silicon

A number of pairs of samples, typically $5 \times 5 \text{ mm}^2$ in size, were cleaved from both processed and unprocessed areas of “epiready” (100) Silicon substrates. One sample from each pair was processed and an identical, unprocessed sample was put through the same photometric analysis to provide normalizing data. Each sample had its edges and back surface coated with protective lacquer so that only the front processed face was exposed to the photometric chemicals.

In order to determine the amount of “free” Silicon, the samples were immersed in 3 ml of concentrated 67% (35.5 N) hydro-fluoride acid. “Free” Si was dissolved from the front surface of each sample by immersion in HF for 30-min. Then the samples were rinsed in distilled water, which was collected and added to HF solution.

Photometrical determination of Si content is based on Si-Mo-acid formation (reduced Si-complex with molybdate of ammonia). The analysis is the same as for As. The optimum value of pH for Si-Mo-acid formation is equal to 2. The discounting influence of F^- -ion excess was eliminated by H_3BO_3 .

In order to determine the boron dopant concentration, the samples were immersed for 5 min. into 5 ml HF:HNO₃ (10:1). This converts boron into the complex anion BF_4^- as HBF_4 . A reaction with dye gives the colored compound $R[BF_4]$ (where R – is the cation of organic dye). This type of compound is easily extracted by a noble organic dye while the dye itself

remains. In summary, the photometrical determination of boron is based on the formation of a triple colored complex $R[BF_4]$ (where R – is the cation of the organic dye - brilliant green – $C_{27}H_{34}N_2SO_4$) and the following extraction by toluol (C_7H_8).

An aliquot of the solution was poured into polyethylene glass. Next, 1-2 drops of brilliant green were added followed by urotropin to neutralize the solution until the blue-green color of the indicator appeared. This solution was then placed into a dividing funnel, 1 ml of 0.5% watered solution of brilliant green and 5 ml of toluol were added and extraction occurred. The toluol layer was photomeasured. The extract was obtained by performing a similar analysis except boron reagents were used as a control solution. Finally, the boron content was determined by using calibration diagrams.

An FEK-56M photometer was used to measure absorbance, with a red (720 nm) filter and a 30-mm working distance used for the Si measurement and an orange (10 nm) filter and a 5-mm working distance used for B determination. For Si and B, concentrations in the final solution over the range 0.1-1.0 $\mu\text{g/ml}$ were measurable, with an accuracy of about 5 %. The masses of free Si and B from each processed sample were normalised for each process studied.

3. Results

GaAs samples after electron beam irradiation :- Optical microscopy data

Optical microscopy of the GaAs surface before and after e-beam irradiation shows that electron beam irradiation generates point defects within the crystal arranged in separated lines. The surface appears homogeneous across the whole sample. This indicates that electron beam irradiation with a 50 nm diameter beam causes defects to propagate across the whole sample surface in a very short period of time (100 s).

GaAs samples after electron beam irradiation :- PCA data.

Standard equipment for electron photolithography was used to irradiate the samples. The value of electron beam current was $I=100$ pA and the accelerating voltage $U=30$ kV. Two 3.5×3.75 mm² samples were cut from the GaAs wafer and irradiated with a 50nm diameter electron beam for 100s and 1000s respectively, Figure 1. The irradiated samples were analysed using Precise Chemical Analysis performed on the irradiated area. Determination of the amount of migrating As atoms is more complicated than Ga due to volatility of As atoms, limiting the accuracy of the method for As. PCA data from these samples obtained by etching in concentrated HCl for 15 minutes is summarized in Table 1 below.

The data clearly shows that significant concentrations of free Ga and As atoms exist at the surface after preliminary treatment and cutting, that is without any electron irradiation. The free Ga to As ratio is $\sim 1:1$ ($t = 0$).

These results suggest that residual stresses due to plastic deformation caused by sample cutting remain in the crystal prior to irradiation. It appears to be an energetically preferable state for the crystal. Although the entropy of the system is known to have increased, the free energy may be lower than for an ideal crystal. This is due to the presence of point defects in the unprocessed crystal [1]. Note that both the free Ga and As amounts reduce with increasing irradiation time.

Silicon wafers after RTD

Proximity rapid thermal diffusion (RTD) is a technique which may be used to dope silicon wafers with boron [6,7]. Spin-on dopant is spun onto a silicon wafer. This dopant source wafer is then stacked in proximity to a bare silicon product wafer using 0.5 mm thick silicon spacers, as shown in Fig. 2.

During RTD, boron trioxide (B_2O_3) evaporates from the spin-on dopant (SOD) at the temperature of $1000^{\circ}C$, across the separation gap to the product wafer, where it is adsorbed onto the surface. Boron diffusion is then accomplished by means of a surface oxidation-reduction reaction between the B_2O_3 and the silicon wafer [8], given by:



In this reaction, doped SiO_2 is formed on the surface of the product wafer and becomes a dopant source for elemental boron, which diffuses into the silicon substrate. Excessive amounts of B_2O_3 can lead to the formation of silicides and other compounds of boron on the silicon surface. This layer often results in device failure due to open contacts.

For our study, Czochralski grown n-type, $\langle 100 \rangle$ oriented, 9-15 Ω cm resistivity silicon wafers were processed using Rapid Thermal Processing to dope the silicon with boron. Each sample was cleaned before the doping process using $H_2SO_4:H_2O_2$ followed by a HF dip. The sample was then rinsed in deionised water.

We used two different SOD compositions (B153 and B155) prepared by Filmtronics (USA). The composition of each SOD is summarized in Table 1 below. The normalized PCA data obtained from our RTP processed samples is summarized in Tables 2 and 3 below.

SEM data

Fig.3 shows the silicon surface after RTD. This surface was etched for 90 s in 50 : 1 HF to remove the B_2O_3 . This image has obvious grain structure. From Tables 2 and 3, the measured “free” silicon and boron content on the surface depends on both the RTD duration and SOD composition

4. Conclusions

We conclude that Photometric Chemical Analysis is a valuable tool for the study of semiconductor surfaces. Using the technique, it is possible not only to determine the surface composition, but also to investigate the consequences of treatment that leads to surface variations.

In particular, it is shown that irradiation with a low-energy electron beam reduces the amount of “free” Ga and As at GaAs surface due to plastic deformation. In the case of RTD the processing increases the amount of “free” silicon at the Si surface and the amount of boron in the near-surface layer due to the spreading of the light energy from the halogen lamps along the grain boundaries.

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Table 1. Ga and As mass (M_{Ga} and M_{As}) vs. duration of e-beam irradiation t .

t , s	0	100	1000
M_{Ga} , μg	20.5	18.1	7.25
M_{As} , μg	21.6	10	2.5

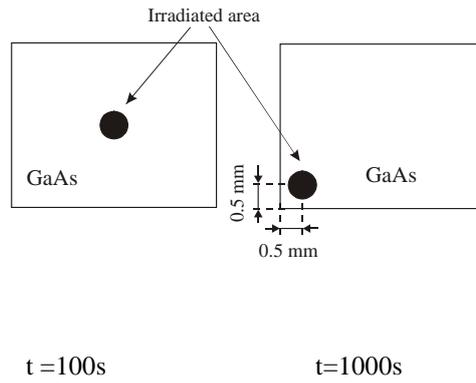


Figure 1. The electron irradiated samples.

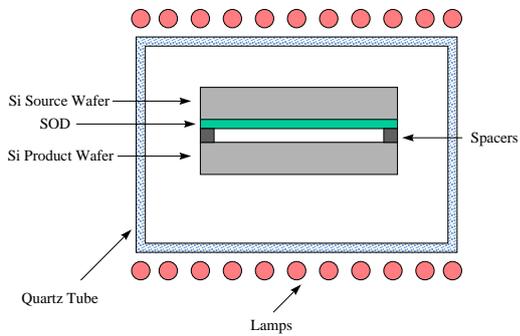


Figure 2. Wafer configuration during Proximity Rapid Thermal Diffusion.

Table 2. Spin on dopant composition.

SOD source	% Dopant Compound	% SiO ₂
B153	2.00	5.0
B155	4.00	0

Table 3. PCA data from RTP processed silicon sample.

SOD source	doping duration, s	B, μ g/cm ²	Si, μ g/cm ²
Reference wafer	0	0	0
B153	30	1.92	5.42
B153	60	1.81	5.05
B155	60	3.65	10.05

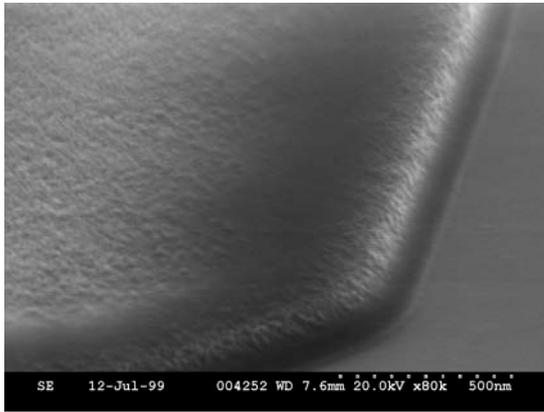


Figure 3. The sample surface after RTD and a 90 s etch in 50 : 1 HF to remove B_2O_3 .