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Gettering of Copper in Ion-Beam Damaged Regions in GaP and GaAs

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Secondary Ion Mass Spectrometry has been used for investigation of accumulation and redistribution of copper in ion implanted GaAs and GaP single crystals. Most copper accumulation takes place at the interface between amorphous region and undestroyed crystal. In GaAs, gettering was observed in the temperature range from 200°C to 700°C. Getter efficiency strongly depends on the annealing process of the implantation damage. In GaP, gettering according to $N_{Cu} \sim \exp(-E_a/kT)$ and $N_{Cu} \sim \exp(bt)$ was found.

§1. Introduction

It is well known, that the presence of fast diffusing metallic impurities (like copper, nickel, and iron) in III-V-compounds even at concentrations as low as $10^{13}cm^{-3}$ leads to a degradation of the functions of the semiconductor devices. Gettering by defects and defect complexes in the bulk, at interfaces and surfaces of the devices is one of the methods for reducing the impurity concentration in the vicinity of electrically or optically active regions. One possibility of introducing defects for gettering is the implantation of electrically inactive or active atoms into the semiconductor material.

§2. Experimental details

For this study we used n-type (Te-doped, $n = 2...5 \cdot 10^{17}cm^{-3}$) GaAs and GaP substrates of (100) orientation. Because of its high diffusivity copper was used for the investigation of the gettering process. To the copper impurity are also related several deep levels in the band gap of GaAs and GaP.[1)]

The experimental procedure was as follow:

(i) Implantation of different ion species (As, Kr, Ga, Ar, P) in the polished front side of the wafers at room temperature with doses to achieve an amorphous layer. To get the implantation peak in the same depth (125 nm in GaAs, 100 nm in GaP) the implantation energy was varied for different ion species.

(ii) Copper vacuum deposition on the back side of the samples. This copper layer serves as an unlimited diffusion source.

(iii) Thermal treatment in an open quartz tube under flowing nitrogen (capless annealing). During this thermal treatment copper diffuses through the sample and is gettered in the damaged region at the front side of the sample.

The measurement of the chemical profiles was performed by Secondary Ion Mass Spectrometry (SIMS) with a CAMECA SMI 300 microanalyser with oxygen primary ion beam and monitoring of the ($^{69}Ga^{63}Cu$) positive ion cluster. Calibration of the atomic concentrations was established by using unannealed copper implantation

profiles as standard. The detection limit of the apparatus for copper (about $2 \cdot 10^{17}$ cm^{-3}) only allows to detect copper contamination in the damaged region because of the lower solid solubility in the undestroyed crystal (less than $2 \cdot 10^{16} cm^{-3}$). The crater depth was measured with a Talystep profilometer. With Rutherford Back Scattering (RBS) measurements it was possible to determine the thickness of the amorphous layer, initially created by the ion implantation.

§3. Results and discussion

Figures 1 and 2 show the concentration profiles of copper for different implanted elements in GaP and GaAs after thermal treatment.

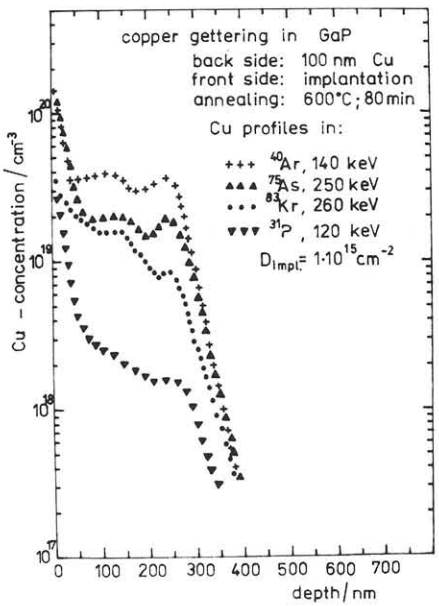

Fig. 1 Copper gettering in GaP.

In the case of GaP most effective gettering was observed for argon implantation[2]. The copper profiles for the Ar, As, and Kr implantation have a similar form: A surface peak, an enrichment of copper near R_p and a peak in a region deeper than $2\ R_p$ are to be seen. It is assumed, that the near surface accumulation is due to the creation of further defects by outdiffusion of phosphorous during during thermal treatment. Because of different copper concentrations in the region around R_p different gettering effects in presence of various complex defect structures in GaP lattice due to different implanted ion species are supposed. The peak near $2\ R_p$ is strongly correlated to the interface between amorphous layer and undestroyed crystal before annealing. From TEM investigations of ion implanted and annealed silicon and GaAs (see for instance ref. 3 and 4) it is known, that in this region rather complicated defects, like loops and stacking faults, are created. This may also be in the case of GaP. These defects can be decorated by Cu. The relative small amount of copper accumulation in the case of phosphorous implantation is probably caused by a better annealing of the radiation damage of light elements.

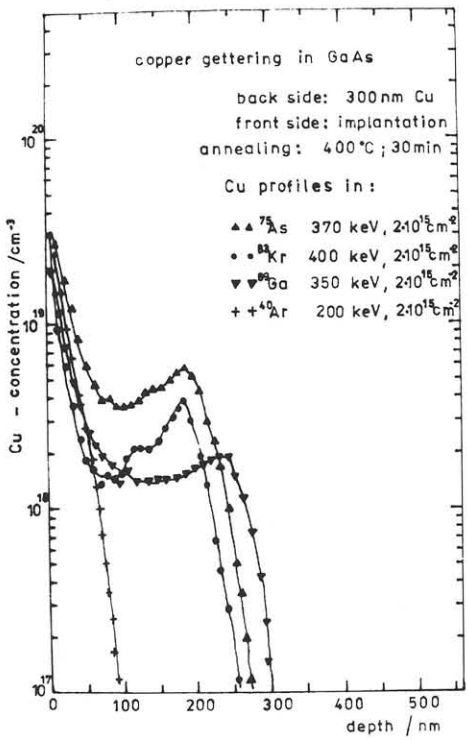

Fig. 2 Copper gettering in GaAs.

As can be seen from Fig. 2 gettering in GaAs is less effective than in GaP (one order of magnitude). The highest getter efficiency in GaAs was observed for arsen implantation. This can be explained as follow. With arsen implan-

tation and following annealing process a relative decrease of Ga is achived. This can also be described by an enrichment of V_{Ga}. In contrast, a gallium implantation would lead to an increase of V_{As}. A krypton implantation wouldn't alter the ratio between arsen and Ga. It seems, that an enrichment of V_{Ga} leads to a better accumulation of Cu in this region by decorating a vacancy (Cu_{Ga}) or a similar complex involving V_{Ga}. All profiles exhibit a second peak in a depth greater than R_p. As like in the case of GaP this peak depth is correlated to the interface between the amorphous layer and undestroyed crystal before thermal treatment. For P and Ar implantations no gettering was observed (Fig. 2). But at lower annealing temperatures (250°C) and also for higher implantation doses ($5 \cdot 10^{15} cm^{-2}$) gettering took place. It seems, that the damage created by implantation of light elements with a relative small dose is annealed at 400°C so that no copper gettering above the detection limit is possible.

Because of an implantation dose dependence of the depth of the second peak it was neither in GaAs, nor in GaP, possible to correlate the copper accumulation in this region with stoichiometric disturbances of host atoms during implantation process as it was calibrated and observed by other authors.[5,6,7] The interface between amorphous layer and undestroyed crystal acts as the most effective gettering trap.

The temperature behaviour of copper gettering in GaAs and GaP is quite different. (Fig. 3 and 4)

In GaAs gettering takes place even at relative low temperatures of about 200°C. The temperature behaviour can be described as a superposition of three processes:

(i) Annealing of defects induced by ion implantation.

(ii) Build up of rather complicated defect structures with annealing procedure due to defect diffusion and mechanical stress at the interface between damaged layer and undestroyed crystal.

(iii) Increase of copper transport through the sample due to higher diffusion coefficient and higher solid state solubility with increasing temperature.

Copper decorates the defects very well. So the first process will lead to a decrease of the getter efficiency, while the second process will increase it.

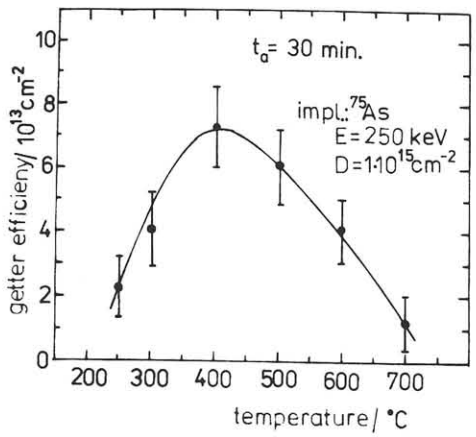

Fig. 3 Getter efficiency (total amount of copper in the gettering region) in GaAs versus temperature.

The increase of the getter efficiency from 200°C to 400°C is due to the priority of processes (ii) and (iii) against the annealing. A further increase of temperature leads to a significant annealing also of rather complicated defects. Copper will migrate to the surface region, which is growing by arsen evaporation and back into the bulk by increased solid state solubility. Consequently, the getter efficiency will be decreased.

The results of the time dependence of gettering agree with the assumption of superposition of the three processes.

The same behaviour was also observed for krypton implantations.

Copper gettering in GaP takes place at higher temperatures.[8]

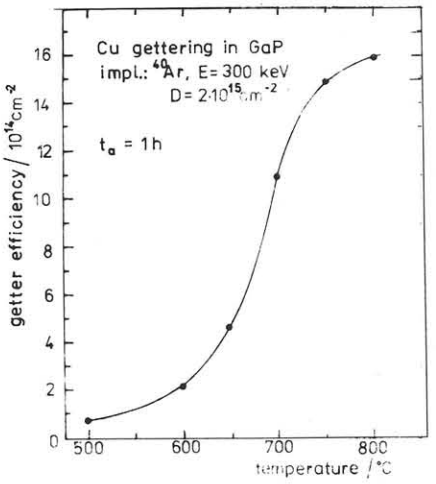

Fig. 4 Getter efficiency in GaP versus temperature.

For the time- and temperature dependence of gettering in GaP was found $N_{Cu} \sim \exp(-E_a/kT)\exp(b\sqrt{t})$. T and t are the temperature and time of annealing, respectively. For $T > 700^{\circ}C$ saturation of copper concentration takes place. It is assumed, that the implantation damage does not anneal at temperatures as low as $750^{\circ}C$. This may also due to the presence of copper in this region. An activation energy of E_a = 1,6 eV and a "diffusion-migration" coefficient of $D_m(600^{\circ}C) = 1 \cdot 10^{-7}$ $cm^2 s^{-1}$ was found. This coefficient is in good agreement with a diffusion coefficient measured by other methods.[9]

§4. Conclusions

The results show, that radiation defects are effective centers for gettering of copper in GaAs and GaP. The highest gettering effect was found for arsen implantations in GaAs and argon implantations in GaP. From the investigations of time- and temperature dependence of gettering it is evident, that in GaAs the annealing and creation of defects play the most important role, whereas in GaP copper diffusion is the dominant process.

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