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Special Issue Paper

Modeling of Copper SIMS Profiles in Thin HgCdTe

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Anomalous secondary-ion mass spectroscopy (SIMS) profiles of copper in thin pieces of HgCdTe are explained using the model used for diode formation by ion milling and ion implantation. In this model, the SIMS ion beam injects mercury interstitials into the HgCdTe as it etches the HgCdTe. The interstitials fill metal vacancies and kick copper off the metal lattice sites. The copper interstitials then diffuse either to the surface being etched, where it is removed and detected by the SIMS instrument, or deeper into the HgCdTe, where it annihilates vacancies. Good agreement between model predictions and experimental SIMS profiles are obtained.

Key words: HgCdTe, secondary-ion mass spectroscopy, copper in HgCdTe, mercury interstitials

INTRODUCTION

It is well established that ion implantation,[1,2] electron cyclotron resonance (ECR) etching, and ion milling[3] can all result in the redistribution of group I impurities in HgCdTe. In all of these cases, the etching or implantation injects mercury interstitials into the HgCdTe. These interstitials diffuse into the bulk of the HgCdTe, either filling metal vacancies, or kicking group I impurities off metal lattice sites. As a result, the group I interstitials diffuse elsewhere, resulting in their redistribution. If there is a residual *n*-type dopant in the HgCdTe, an *n*-type region will be created, resulting in the formation of a p–n^- junction.

SIMS profiling is very similar to ECR and ion mill etching. In place of the blanket etch in these techniques, the SIMS instrument uses a raster-scanned ion beam, although at a somewhat higher energy (~8 kV). The SIMS erosion process is expected to also result in the injection of mercury interstitials into the HgCdTe, and thus have an effect on the impurity distribution. Indeed, this has been demonstrated for the case of gold in HgCdTe.[4]

In this work, we report on modeling of the SIMS profile of copper in thin, ~8 μm thick HgCdTe. Because of the prior thermal history of these samples, the copper is expected to be uniformly distributed throughout the HgCdTe. The SIMS profiles do not show this. To explain the results, a model previously used to describe the junction formation process is applied to the actual profiling in the SIMS instrument.

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EXPERIMENTAL

In this work, long-wave infrared (LWIR) HgCdTe grown from a tellurium-rich melt by liquid-phase epitaxy (LPE) was used. The HgCdTe was thinned to ~8 μm and passivated with interdiffused CdTe on both top and bottom surfaces. A schematic of the sample configuration is shown in Fig. 1. The HgCdTe samples were doped with 1×10^{16} cm^{-3} to 2×10^{16} cm^{-3} copper. The interdiffusion process involves a 4 day anneal under N_2, equivalent to an anneal under tellurium-rich conditions. At the conclusion of this anneal, the copper is expected to be uniformly distributed throughout the HgCdTe. In addition to the copper acceptors, ~1×10^{16} cm^{-3} metal vacancies should be present.[5] Hall carrier concentration and device measurements are consistent with this conclusion.

Pieces of this material were subjected to SIMS profiling using an O_2^+ ion beam.

RESULTS AND MODEL

A typical profile obtained is shown in Fig. 2. We have seen similar profiles in all four of the thin copper- and vacancy-doped samples that we have

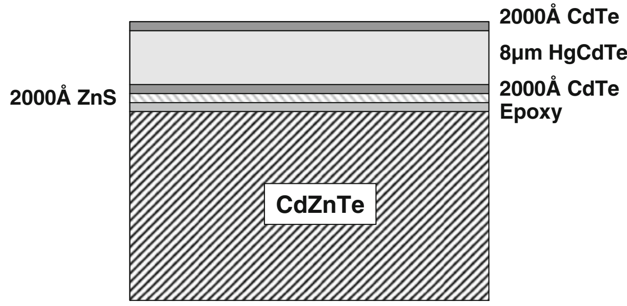

Fig. 1. Schematic of samples used in experiments.

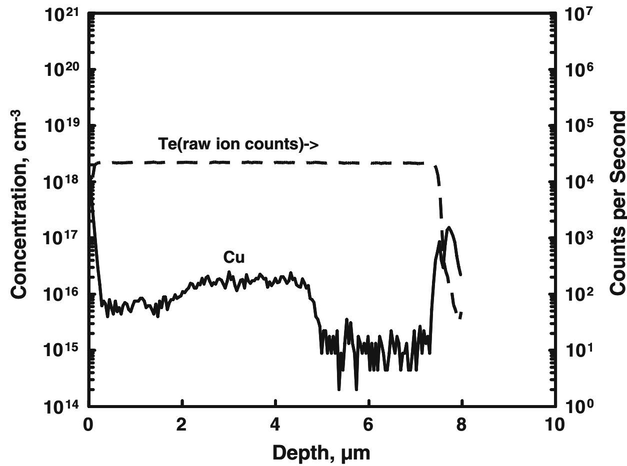

Fig. 2. SIMS profile of copper in a 7.5 μm thick layer of HgCdTe.

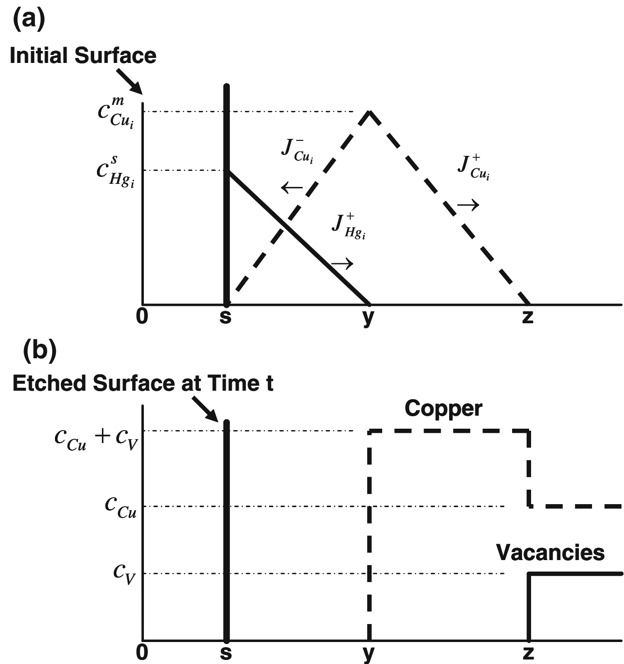

Fig. 3. Junction formation model. The *x*-axis is the depth into the sample. *s* is the depth of the etch, *y* is the junction depth, the depth to which copper and vacancies have been depleted, and *z* is the depth to which the copper interstitials freed during the etch process have filled metal vacancies. (a) Profile of interstitials in HgCdTe during etch processes. Interstitial fluxes are also shown. (b) Copper and vacancy concentrations in HgCdTe during etching.

had analyzed. We do not see this type of profile in thick (>30 μm) copper- and vacancy-doped samples. In this 7.5 μm thick film, the copper concentration in the surface CdTe passivation is $\sim 10^{18}$ cm^{-3}. In the HgCdTe, it drops rapidly to 8×10^{15} cm^{-3}, and then increases to $\sim 2 \times 10^{16}$ cm^{-3} ~ 2.5 μm into the film. At ~ 4.5 μm, the copper concentration drops to the background level and stays at this concentration through the remainder of the HgCdTe film. It then rises to $\sim 10^{17}$ cm^{-3} in backside CdTe passivation and ZnS. While different copper concentrations in the CdTe, ZnS, and HgCdTe films are to be expected as a result of different chemical activities, the reported nonuniform distribution of copper in the HgCdTe film is in conflict with the uniform distribution that is expected to result from the prolonged interdiffusion anneal.

An explanation for this unexpected profile can be found by applying a model similar to that used for the formation of *p*–*n* junctions in the HgCdTe during ECR etching or ion implantation. In this model, the SIMS ion beam injects interstitials into the HgCdTe during the profiling. These interstitials diffuse into the HgCdTe as shown in Fig. 3, kicking out the copper and filling vacancies. This leads to a region near the surface where the HgCdTe is depleted of copper, depicted in Fig. 3b. The copper interstitials generated by this process diffuse either to the surface being etched or deeper into the HgCdTe where they combine with metal vacancies. The copper that diffuses to the surface is removed by the etch process, and gives rise to the SIMS signal. As the profiling continues, all of the vacancies in the HgCdTe are eventually filled. There being no other place for these interstitials to go, assuming the backside cannot act as a sink, all of the copper interstitials must then diffuse to the front surface. This gives rise to an increase in the SIMS signal. As the profiling continues even further, all of the copper in the HgCdTe is removed, but HgCdTe still remains. This results in the SIMS copper signal dropping to the background, even though there remains some HgCdTe. The mathematical details of this model are developed in the appendix.

Quantitative modeling of this process has been done using the model in the Appendix. It was assumed that the mercury and copper interstitial diffusion coefficients were the same, and were equal to that estimated by Melendez and Helms[6]:

$$D_{\mathrm{Hg_i}} = 2.35 \times 10^{-3} \exp\left(-\frac{0.15}{kT}\right)$$

The sample was assumed to be at 300 K. It was found that the best fits were obtained using the model in which the surface concentration of mercury interstitials was fixed. A typical result is

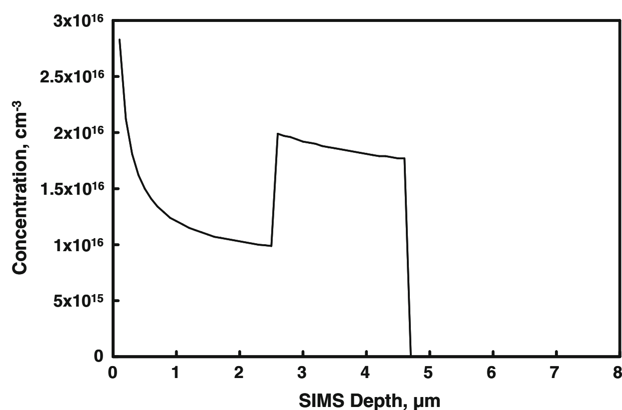

Fig. 4. Modeled copper profile in a thin HgCdTe layer. The initial copper concentration in this profile was taken to be 10^{16} cm^{-3}, uniformly distributed throughout the film.

shown in Fig. 4. For this calculation, the erosion rate, R_{HgCdTe}, was taken as 70 Å s^{-1}, the bulk vacancy concentration was assumed to be 6×10^{15} cm^{-3}, the bulk copper concentration was taken as 10^{16} cm^{-3}, and the surface concentration of mercury interstitials was taken as 5×10^{11} cm^{-3}.

The calculation reproduces the general features of the experimental profile. There is an initial peak in the copper concentration due to very large interstitial gradients at the beginning of the etch process. This leads to a large flux of copper diffusing to the surface, and a rapid depletion of copper near the surface itself. As etching progresses, the SIMS concentration subsides to a value close to the original bulk concentration. As the vacancy boundary, z, touches the backside of the sample, which occurs when the SIMS etched depth is ~2.5 μm, the SIMS concentration increases to ~2 times the original bulk concentration. This is a result of the now higher copper concentration in the back part of the bulk—a concentration equal to the original copper concentration plus the original vacancy concentration—and the fact that, with no vacancies left, all copper that is kicked off lattice sites can only diffuse to the front surface. Finally, when the junction, y, reaches the backside, all copper has been removed from the sample. The SIMS concentration therefore drops to the noise background. This occurs when the SIMS etch depth is ~4.5 μm.

DISCUSSION

The modeled profile replicates the general features of the measured SIMS profile. The initial surface spike in Fig. 2 is largely an artifact of the SIMS measurement itself, arising as the SIMS erosion process attains a steady state. This effect is not modeled in Fig. 4. The peak that is shown in this figure is much smaller (the concentration axis of this figure is linear, not logarithmic as in Fig. 1) and is largely covered up by the nonequilibrium process. As the initial spike disappears, the SIMS concentration that is modeled approaches the copper concentration in the sample. In very thick samples this is what is observed both experimentally and in the model. A steady state is reached in which the flux of copper interstitials to the surface reflects the actual concentration, while the remainder snow-plow into the material, filling additional vacancies deeper in the HgCdTe. The elevated copper concentration is eventually seen when there is no longer any sink for the copper interstitials except for the front surface of the sample.

The two main factors that lead to disagreement between the experimental and modeled profile are probably (1) the breakdown of the approximation of planar etching for the rastered SIMS etching, and (2) the assumption that the back CdTe-HgCdTe interface cannot sink copper interstitials. Although the detailed erosion-diffusion process is much more complicated in the real rastered SIMS profile than in the blanket erosion process model, it can be argued that the blanket model should give a fairly decent approximation of the SIMS measurement. Assuming a SIMS beam area of ~10 μm^2 and a raster ~100 μm on a side, the instantaneous erosion rate beneath the beam would be three orders of magnitude greater than the average rastered erosion rate. Mercury and copper interstitials produced below the beam would diffuse laterally a distance equal to a few times the depth y to which copper has been removed. As the beam moves, these effects should average out, leading to a profile similar to that obtained by a uniform blanket etch process, particularly since raster edge effects are eliminated by sampling only in a much smaller region within the overall raster. There is also the possibility that copper interstitials are "gettered" into the passivation-HgCdTe interface at the back of the sample, although this should occur only after the vacancy boundary, z, reaches the backside of the HgCdTe film.

The general agreement between the modeled and experimental data also lends support to the model for diode formation in high-density vertically interconnected photodiode (HDVIP™) arrays. In particular, it validates the observation that metal vacancies are annihilated not only in forming the n-type region of the diode, but in the p-type region as copper interstitials migrate into the p^+ region. The result is a reduced metal vacancy concentration in the unit cell and a reduced dark current from these defects.

It is also remarkable that the SIMS profile does not show the true distribution of the copper in the film. In fact, the model argues that the copper concentration in the HgCdTe immediately beneath the beam is ~0. The copper that is profiled comes from much deeper within the film.

APPENDIX

Figure 3 shows the pertinent parameters for the model. In general, the continuity equation for mercury interstitials is given by:

$$\frac{\partial c_{\mathrm{Hg_i}}}{\partial t} = \frac{\partial J_{\mathrm{Hg_i}}}{\partial x} - \Phi \quad (1)$$

where Φ is the rate of annihilation or creation of mercury interstitials. Between s and y, $\Phi = 0$. It is assumed the concentration of interstitials is always small ($\lesssim 10^{12}\ \mathrm{cm^{-3}}$) in comparison to the concentration of copper or vacancies in the region to the right of y ($>10^{15}\ \mathrm{cm^{-3}}$). Under these circumstances, we can assume a steady-state solution in the region between s and y, and set the left-hand side of Eq. 1 equal to zero. The incoming flux of mercury interstitials is then

$$J_{\mathrm{Hg_i}} = -D_{\mathrm{Hg_i}} \frac{\partial c_{\mathrm{Hg_i}}}{\partial x} = -D_{\mathrm{Hg_i}} \frac{c^{\mathrm{s}}_{\mathrm{Hg_i}}}{y - s} \quad (2)$$

where $D_{\mathrm{Hg_i}}$ is the mercury interstitial diffusion coefficient.

The incoming mercury interstitials annihilate vacancies and kick out copper atoms, causing the junction, y, to move deeper into the solid:

$$J_{\mathrm{Hg_i}} \mathrm{d}t = (c_{\mathrm{V}} + c_{\mathrm{Cu}}) \mathrm{d}y \quad (3)$$

The copper interstitials that result from the kick-out mechanism diffuse either to the surface, $J^{-}_{\mathrm{Cu_i}}$, or into the solid, $J^{+}_{\mathrm{Cu_i}}$, to occupy existing metal vacancies:

$$J^{-}_{\mathrm{Cu_i}} = D_{\mathrm{Cu_i}} \frac{c^{\mathrm{m}}_{\mathrm{Cu_i}}}{y - s}; \quad J^{+}_{\mathrm{Cu_i}} = D_{\mathrm{Cu_i}} \frac{c^{\mathrm{m}}_{\mathrm{Cu_i}}}{z - y} \quad (4)$$

The concentration of copper interstitials at y, $c^{\mathrm{m}}_{\mathrm{Cu_i}}$, will be that required so that the two copper interstitial fluxes equal the incoming mercury interstitial flux:

$$J_{\mathrm{Hg_i}} = J^{-}_{\mathrm{Cu_i}} + J^{+}_{\mathrm{Cu_i}} \quad (5)$$

For the case when z is less than the sample thickness, the SIMS concentration will be given by

$$\mathrm{Cu} = \frac{J^{-}_{\mathrm{Cu_i}}}{R_{\mathrm{HgCdTe}}}; \quad s = R_{\mathrm{HgCdTe}} t \quad (6)$$

where R_{HgCdTe} is the HgCdTe etch rate. Once z equals the film thickness, $J^{+}_{\mathrm{Cu_i}}$ falls to zero, $J^{-}_{\mathrm{Cu_i}}$ and becomes equal to $J_{\mathrm{Hg_i}}$. Thus

$$\mathrm{Cu} = \frac{J_{\mathrm{Hg_i}}}{R_{\mathrm{HgCdTe}}}; \quad s = R_{\mathrm{HgCdTe}} t \quad (7)$$

Finally, when y equals the film thickness, all copper has been removed from the sample, and the SIMS concentration falls to zero.

Constant Surface Concentration

This is the case where the etching establishes a constant interstitial concentration, $c^{\mathrm{s}}_{\mathrm{Hg_i}}$, at the surface. This has been found to be the best fit for the case of interstitials released during annealing of ion implantation damage. If the etched depth, s, is small in comparison with the junction depth, Eqs. 1 through 5 may be solved to give

$$y = \sqrt{\frac{2c^{\mathrm{s}}_{\mathrm{Hg_i}} D_{\mathrm{Hg_i}} t}{(c_{\mathrm{V}} + c_{\mathrm{Cu}})}}, \quad z = \sqrt{\frac{2D_{\mathrm{Hg_i}} c^{\mathrm{s}}_{\mathrm{Hg_i}} t}{c_{\mathrm{V}}}} \quad (8)$$

In general for the SIMS case, s is not small, and numerical calculation is required.

Constant Injection Rate

This is the case when the incoming flux of mercury interstitials remains fixed in time, $J_{\mathrm{Hg_i}} = J$. This case has been found to provide the best description for the case of interstitials generated during ion milling or ECR etching. If the etched depth, s, is small in comparison with the junction depth, Eqs. 1 through 5 may then be solved to give in the limit when $z \gg y$:

$$y = \frac{Jt}{(c_{\mathrm{V}} + c_{\mathrm{Cu}})}, \quad z = \frac{Jt}{\sqrt{c_{\mathrm{V}}(c_{\mathrm{V}} + c_{\mathrm{Cu}})}} \quad (9)$$

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