MODELLING OF OXYGEN PRECIPITATION AND OUTDIFFUSION PHENOMENON

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KEY WORDS: diffusion, oxygen precipitation, oxygen nucleation, critical radius, numerical simulation

ABSTRACT: On the basis of the diffusion-controlled precipitation of spherically growing particle, homogenues nucleation and classical diffusion theory and simplified expression for the critical radius, which takes into account only temperature dependence, a PASCAL program to run on IMB PC was written to simulate nucleation, precipitation and outdiffusion phenomenon. The parameters we need for simulation were deduced from already published two step annealling experiments. Diffusion constant, D = 0.07 exp (-2.44/kT) /7/, was found to be adequate for the temperatures above 1073 K. For the lower ones enhanced diffusivity should be assumed. The results of the numerical simulation of various IME's and other published processes are in good agreement with the experimental ones, not only for the amount of precipitated oxygen at various steps, but for the depth of the denuded zone and the defect/precipitate density as well.

MODELIRANJE PRECIPITACIJE IN OUTDIFUZIJE KISIKA

KLJUČNE BESEDE: difuzija, precipitacija kisika, nukleacija kisika, kritični radij, numerična simulacija

POVZETEK: Na osnovi teorije difuzijsko omejene precipitacije sferično rastočega izločka, teorije homogene nukleacije, klasične difuzijske teorije in poenostavljenega izraza za kritični radij, ki upošteva le temperaturno odvisnost, je bil napisan program, ki simulira pojav nukleacije, precipitacije in difuzije kisika s površine rezine. Za simulacijo potrebni parametri so bili določeni na osnovi objavljenih 2 stopenjskih poskusov. Na temperaturah nad 1073 K je difuzijska konstanta 0.07 exp (-2.44 eV/kT) ustrezna, za nižje pa je potrebno upoštevati ojačeno difuzijo. Rezultati simulacije precipitacije kisika za IME procese, kakor tudi za v literaturi objavljene se dobro ujemajo z izračunanimi.

INTRODUCTION

VLSI devices are mostly processed on CZ Si wafers with oxygen concentration ranging from $5x10^{17}$ - 10^{18} at/cm^3. Precipitation of SiO phase occurs /1/ as a result of exceeded solid solubility limit at almost all process temperatures. Secondary defects like stacking faults etc. which are more or less electrically active are generated at the oxygen precipitates. Especially defects decorated by heavy metals located in the device active area /2/ can be harmful for the functionallity of the IC. On the other side those ones located in the bulk act as gettering centers and have very beneficial effect on the device yield.

To assure the maximum yield for the certain process the intrinsic gettering (IG) should be optimised. To avoid an extensive number of costly experiments, one should be able to model the precipitation and outdiffusion of oxygen for various heat treatments.

In this paper a simple PASCAL program to run on IBM PC is presented in which the diffusion-controlled precipitation of growing spherical particle /3/, homogenues nucleation theory /4, 5/ classical diffusion theory /6/ and simplified expression for the critical radius /7/, taking into account only temperature dependence are combined. Calculated results are compared with the published ones for two step precipitation experiments as well as for the different in /8/ and out of house processes and show a good agreement not only for the amount of precipitated oxygen, but for the depth of the denuded zone (DZ) and precipitate density as well.

2. THEORY

The formation of the denuded zone depends on the diffusion and precipitation (which depends on diffusion) of interstitial oxygen (O_i). Diffusion can be drescribed by classical equation

$$\frac{dO_i(x,t)}{dt}=D(T)\frac{d^2O_i(x,t)}{dx^2} \quad (1)$$

where the diffusion constant defined by Mikkelsen /9/ is (21)

$$D(T) = 0.07\ (cm^2/s)\ \exp\ (-2.44\ eV/kT) \quad (2)$$

To solve the equation (1) the boundary conditions should be known. As the mass transport coefficient h at the surface is not known, we kept the same conditions as in the originally written program /6/. Diffusion controlled precipitation can be, in a very accurate way, described with Ham's theory /3/, which in the simplest form takes into account the growth of a spherical particle. Relation between precipitated oxygen fraction Sp(t) and cinetic constant K (x,t) is quite complicated:

$$K\ (x,t) = H\ (Sp^{\ 1/3}) \quad (3)$$

$$Sp(t) = (O_i\ (x,0)-O_i\ (x,t))/(O_i\ (x,0) - O_i^*\ (T)) \quad (4)$$

$$H(u) = (1/2)\ \ln\ ((u^2+u+1)/(u^2-2u+1))-3^{1/2}\ \mathrm{artg}\ ((2u+1)/3^{\ 1/2}) + 0.9068 \quad (5)$$

Cinetic constant in our program is defined by the following expression:

$$K(x,t=0)=D(T)(4\pi N_o)^{2/3}\ 3^{1/3}\ ((O_i\ (x,0)-O_i^*\ (T))/C_o)^{1/3} \quad (6)$$

where C_o denotes oxygen concentration in a precipitate ($C_o = 4.65x10^{22}$ at/cm^3 for amorphous SiO_x). For the solubility of oxygen O_i^* (T) we used Craven's data /10/.

We applied homogeneous nucleation theory /4,5/ in which the nucleus density N_o is described by the following equation:

$$N_o(x,t) = J_s(x,T)(t-t_i)(1-\exp(-t/t_i)) \quad (7)$$

$$J_s(x,T) = J_oD(T)\ O_i(x,0)\ T^{-1/2}\ \exp(-E_o/(T-T/T_s)^2) \quad (8)$$

$J_o=7.94x10^{-11}$ cmK$^{1/2}$ and $E_o=1082$ K are material constants estimated in /5/, while t_i denotes incubation time in which the nucleus grows during the low temperature nucleation step up to the critical radius $R_c$defined by high temperature precipitation step and T_s the solubility temperature when O_i(x,)) equals solubility O_i^*(T).

Expression for the critical radius R_c originally obtained by C. Claeys /7/ is rather complicated. We used simplified expression, where the elastic, intersticial and vacancy energy term were neglected. From the literature /11/ it is known that the concentration of the point defects at the typical process temperatures and the amount of precipitated oxygen is close to the equilibrium ones. Furthermore during the low temperature (T=1073 K) formation of platelike precipitates no intersticials are emitted. On the other side during the high temperature annealing (T> 1373 K) the precipitation of octahedral precipitates is accompanied by strong emmision (0.69I int./at) of interstitials and succesive growth of stacking faults. We were satisfied to incorporate neglected energy terms in "effective" interface energy σ_{eff}, determined from the two step experiments. The simplified expression for Rc is:

$$Rc = \frac{2\ \sigma_{eff}}{3CpkT\ln(Oi\ /Oi^*\ (T))} \quad (9)$$

Cp is silicon concentration in SiO_2 precipitate and equals $2.1x10^{22}$/cm^3.

The output of the complete calculation is therefore:

* the profile of the interstitial oxygen Oi
* the profile of the precipitated oxygen
* the amount of the precipitated and outdiffused oxygen
* the density of the precipiates and its average size.

3. RESULTS

As the first step the σ_{eff} was determined on the basis of published two step experiments /12/. (2h @ 1073 K + 16h @ 1323 K, N_2 + 5% O_2). The best fit of the experimental results for the amount of precipitated oxygen versus initial concentration O_i presented in fig. 1 is obtained assuming Rc = 7.5 nm at 1323 K and for O_i = $7x10^{17}$ at/cm^3. It follows from (9), that in this case σ_{eff} equals 5.60 J/m2, which is for one order of magnitude higher than the published data for σ /14/. Obviously very crude assumption is made neglecting elastic energy term. Regardless of the assumption, the results for simulated CMOS process /12/, (5h @ 1198 K, O_2 + 45 min @ 1073 K, N_2 + 20h @ 1423 K, N_2 + 14h @ 1198 K, steam), shown on the same fig. 1 are in a very good agreement with the calculated ones.

Nucleation simulation at the temperatures less than 1073 K is not satisfactory, unless the enhanced diffusivity is assumed. Results for amount of precipitated oxygen at two step experiment /13/ with nucleation step performed at 1023 K for 4h (second step is the same as in the first case) are shown in fig. 2. Obviously one can get a good fit assuming 1.5 times higher oxygen diffusivity when the calculated results lie within the statistical limits of the experiment. From some papers (eg. /14/ it follows that at the low temperatures oxygen diffuse in molecular form, so the Mikkelsen data /9/ are too low. Otherwise oxygen precipitates at low temperatures in platelike form, while we supposed the simple spherical form.

The depth of the denuded zone in simulations is set to be where the concentration of precipitated oxygen is 0.25×10^{17} at/cm^3, that guarantees the best correspon-

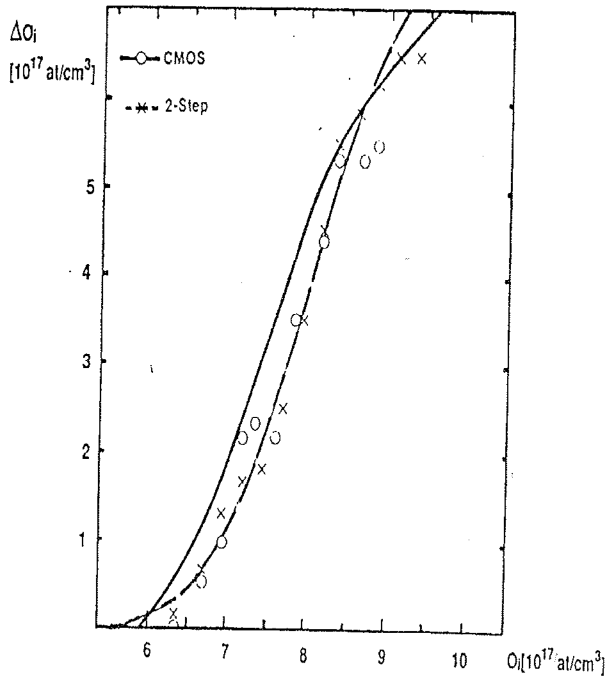

Figure 1: The average amount of precipitated Op vs. initial oxygen concentration O_i @ for the two step (x) and CMOS (o) simulation. Solid lines are calculated.

dence of the results of other simulations /6/ and experiments. Comparison with the results of three step experiment /6/ (1373 K + @1023 K + 1273 K for different times) is shown in fig. 3. while an example of calculated oxygen profile is shown in fig. 4.

4. SIMULATION OF ISKRA - ME'S PROCESS

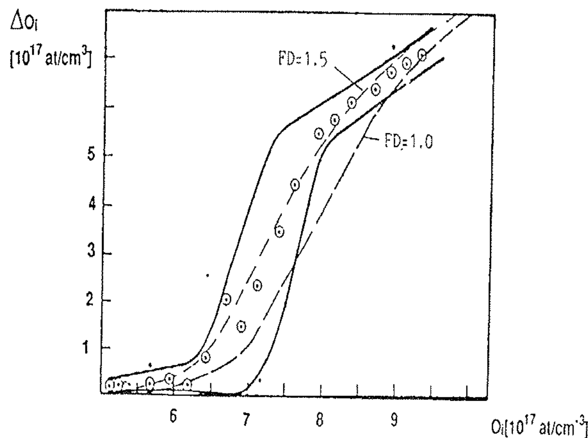

Figure 2: The average amount of precipitated Op vs. initial oxygen concentration O_i @ for the two step experiment. Dotted lines are calculated, while the solid ones represent statistical limits.

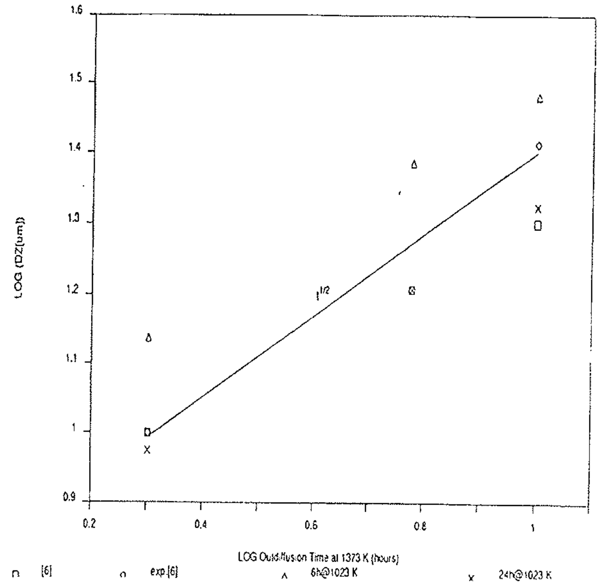

Figure 3: DZ width depending on outdiffusion time for the three step test. (1373 K + 1023 K + 8 h @1273 K, $O_i = 8 \times 10^{17}$ at/cm^3).

Typical ISKRA-ME'S process is run on 100 mm CZ silicon wafers with interstitial oxygen concentration $O_i = (6\text{-}8) \times 10^{17}$ at/cm^3, which sometimes ($O_i < 7 \times 10^{17}$ at/cm^3) shows a lack of intrinsic getterin during the first steps, which results in high density of OSF, and consequently soft p-n junctions. Due to the shortage of wafers with wide oxygen interval we were forced to perform simulations using described program.

Experimental results (IR measurement of O_i, etched cleavage planes for depth of DZ and calculations are shown in fig. 5 and 6. In fig. 5 which represents the concentration of O_i during process steps up to gate oxydation one can see quite good correlation between experiment and calculation for wafers with medium concentration. One can also see, that for low oxygen concentration there is almost no visible precipitation (only outdiffusion) what results in lack of IG. For high oxygen

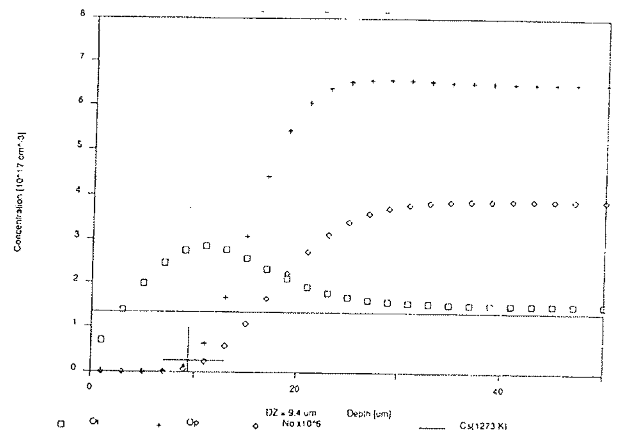

Figure 4: Calculated profiles of interstitial (O_i) precipitated (O_p)oxygen and of precipitate density N_O for the three step test. (2h @ 1373 K + 24 h @1023 K + 8 h @ 1273 K, $O_i = 8 \times 10^{17}$ at/cm^3).

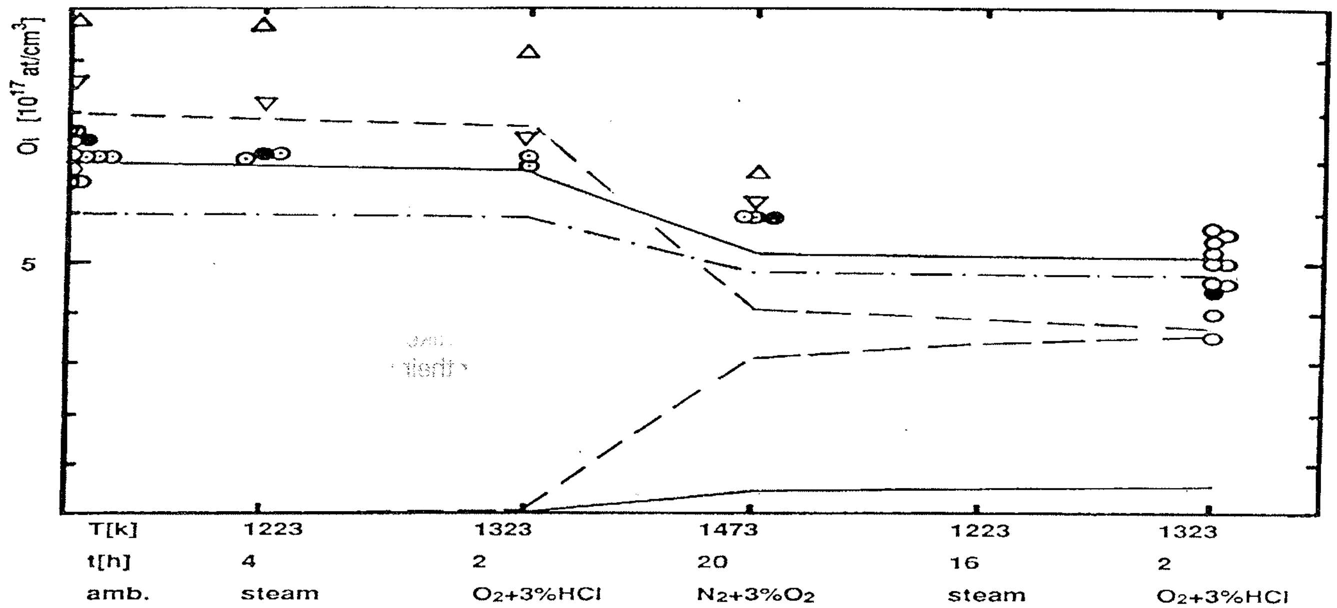

Figure 5: **Measured and calculated interstitial and precipitated oxygen concentration during ISKRA-ME's CMOS process.**

Figure 6: **Final experimental and calculated results for ISKRA-ME'S CMOS process.**
a) DZ widht vs. initial interstitial oxygen (O_i) concentration.
b) Change of the interstitial oxygen O_i and precipitated oxygen (Op) concentration vs. initial concentration.

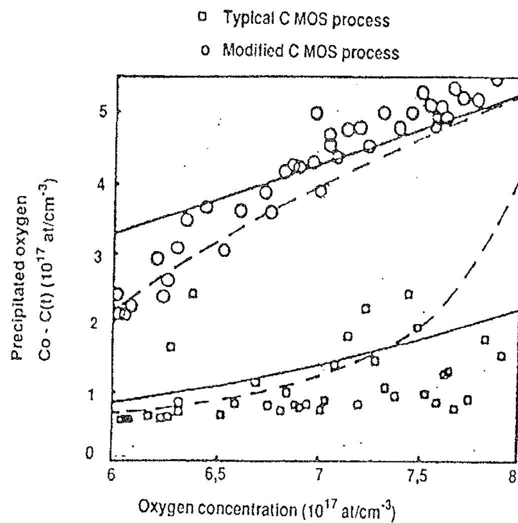

Figure 7: **Precipitation of oxygen in CMOS process /5/. Our calculations are represented by dotted lines. Modified process was treated for 4h at 973 K before processing.**

concentration one can see that the main change in O_i is during diffusion step. But most probably the amount of precipitated oxygen is overestimated at 1473 K.

The depth of DZ and change in O_i concentration after the last step is shown in fig. 6. for the standard and modified process (an extra nucleation after diffusion step). It is clear that the calculated results for precipitation are somewhat overestimated, most probably at the diffusion step, meanning that the R_c at 1473 K is higher than our assumption which is more realistic because the density of precipitates is lower than calculated one at diffusion step for very high oxygen content, or that the solubility at this temperature is higher then Craven's data /10/. With black dots are also shown the results for the fast precipitated material presented by black dots in Fig.6, which could be simulated assuming one hour nucleation step at 1073 K before the first process step. On the other side the outdiffusion step, before processing, increases DZ depth, what can be important for material with very high oxygen content.

On the same way we simulated same other in and out of house processes. Our calculations were always within expermental statistical limits for the final oxygen concentration for the certain process. An example for experimental data in /5/ is shown in fig. 7.

5. CONCLUSION

A quite simple program for IBM PC which simulates outdiffusion, precipitation, and nucleation of interstitial oxygen in CZ silicon was written. Regardless of the crude assumption for the critical radius and limitation to spherical geometry the results are realistic. Dissolution of precipitates and diffusion of self interstitials from the surface should be incorporated in future, as well as implementation of the formulas for growth of platelike precipitates during low temperature nucleation steps.

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