In a foregoing paper /1/ it was shown that the formation of substitutional transition metal (TM) defects M₄ in silicon float zone (FZ) crystals can be interpreted with the Frank-Turnbull (FT) reaction. Experimental results were presented for the metals Cu, Ni, Co, Ag, Pd (group I) and Rh, Au, Pt, Ir (group II). Using a simplified solution of the FT-differential equation it could be shown that the frozen-in process of the defects M₄ takes place near a characteristic temperature Tₑ, which is mainly determined by the binding energy E₀ of the defects on lattice sites. For low E₀ = 2 eV, as for the dopants Cu and Ni, Tₑ = 1000 K holds. But the formation of substitutional defects is not the only defect reaction which takes place during the crystal cooling process. Due to high concentrations of interstitial defects Mᵢ in particular for dopants of group I, additional pairing reactions according to Mᵢ-Mᵢ (including complexes with multiples of Mᵢ) have to be expected. Indeed a strong influence of pairing reactions was previously observed for all dopants of group I in FZ crystals grown in argon atmosphere (B-crystals) /2/.

The present paper reports on new experimental and theoretical results characterizing the pairing behavior of these metals. Deep level transient spectroscopy (DLTS) was used to identify the substitutional defects M₄ via their characteristic gap levels and to determine their concentrations. The pair defects Mᵢ-Mᵢ, however, showed no DLTS signatures except for Cuₙ-Cuₙ with an energy level at Eᵦ ≈ 0.1 eV. Therefore the degree of pair formation could be concluded only indirectly from the reappearance of the deep levels belonging to Mᵢ defects after appropriate annealing leading to pair dissociation. For dislocation-free crystals grown in vacuum (A-crystals) a complete pairing took place. In dislocated crystals, on the other hand, only isolated substitutional Cu-defects could be detected.

It is shown that this strongly deviating behavior can be explained with different precipitation coefficients R = Nᵢ exp(∆E/kT) of the defects Mᵢ in the temperature range of supersaturation T < 1000 K to 1100 K, where D is the diffusion coefficient of the defects Mᵢ and Nᵢ is the effective density of precipitation sinks such as dislocations or microdefects. For Cu, Ni and Co strong pairing reactions were also observed in dislocated B-crystals. It is most probable that this peculiarity is caused by the high hydrogen content due to humidity traces in the argon ambient /3/. The hydrogen content in the range 10¹⁵ cm⁻³ leads evidently to a hindered activity of the precipitation sinks in B-crystals. Knowing the precipitation coefficient R(T) and the mass action constant K(T) = Nᵢ exp(-Eᵦ/kT) the formation rate of the transition metal pairs during the crystal cooling process can be easily calculated, where Nᵢ is the concentration of lattice sites, Eᵦ is the binding energy and k denotes the Boltzmann constant. It is shown that the mathematical methods as published in /1/ for the calculation of the concentration Nᵢ(0) can be also used for the determination of the frozen-in concentration Nᵢ(0) of the TM pairs.

The important parameters Eᵦ and R were determined by annealing experiments in the dissociation range of the different TM pairs. For the measurement of the isochronal (t = 10 or 20 min) annealing curves Nᵢ(0) = f(T) samples of nearly the same axial position in the FZ crystals were chosen using for each temperature a new sample. After annealing the concentration of isolated defects M₄ was measured by DLTS at different depths of the samples. The results for Ag are shown in Fig.1 for the depths 20 and 500µm. The strongly enhanced reaction rate at d = 20 µm is caused by diffusion processes near the surface. More detailed investigations of the profiles in n-type crystals showed that the diffusion of vacancies and self-interstitials is important for this behavior. For the interpretation of the annealing results it is assumed that simultaneously to the dissociation of the pairs a precipitation of the interstitial defects takes place, which is strongly influenced by the transport of intrinsic point defects. Hence, a simple theoretical model could be derived at time only for the bulk regions using the following assumptions:

1. The total concentration Nᵢ of the defects Mᵢ, at t = 0 equals that of the pairs.
2. Due to the high diffusivity of the defects Mᵢ at the annealing temperature T it is only possible to detect at each time only the concentration Nᵢ(0) = Nᵢ(T) - Nᵢ(T) at room temperature.
3. The transport of the interstitial defects during precipitation is governed by an effective diffusivity according to Dₑ = Dexp(K(T)/K(T) + Nᵢ(T)).
4. During the precipitation reaction the concentrations are in a quasi-equilibrium state according to Nᵢ(T) = Nᵢ(T) / K(T) + Nᵢ(T).

With these assumptions a simple analytic solution could be derived, which allows determination of the parameters Eᵦ and R for the bulk regions provided that the migration energy W of the defects Mᵢ is known. Using published data of W the following binding energies of the pairs were found: 1.1 eV for Cu, 1.7 eV for Ni, 2.0 eV for Co, 1.7 eV for Ag, and 1.9 eV for Pd. The cited precipitation coefficients in Fig.1 were calculated for the temperatures Tₑ belonging to Nᵢ(T) = Nᵢ(T) / 2. The experimental results at d = 20µm are characterized by a much higher precipitation rate and an additional energy ΔE. Both features are obviously caused by the diffusion processes. The curves were calculated with the analytic solution of the reaction equation using the cited parameters.