Comment on "Quantitative analysis of annealing-induced structure disordering in ion-implanted amorphous silicon," by Ju-Yin Cheng *et al.*, J. Vacuum Science and Technology A 20, 1855 (2002)

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In an article recently published in this Journal, Cheng *et al.*[1] presented fluctuation electron microscopy (FEM) measurements which they attributed to variable medium-range order (MRO) in amorphous silicon. Furthermore, they claimed that a strong correlation exists between the changes in MRO and "thermal relaxation," the term they used to identify structural relaxation in amorphous silicon. One of the manifestations of structural relaxation is a considerable heat release upon first-time annealing, up to 40% of the heat of crystallization, and although the authors did not quantify how much heat would be released by the reduction in MRO, they did state that the paracrystalline state can "liberate a great amount of free energy, too".

The only justification put forward to correlate a heat release with changes in the MRO is the similar value of the activation energy of 2.2 eV as measured for changes in the FEM variance[1] and as quoted for the heat release upon structural relaxation.[2] However, in Ref. 2 the value of 2.2 eV is never mentioned as *the* activation energy of structural relaxation. Rather, the heat release is characterized by a wide spectrum of activation energies, and when a measurement is performed at 500 °C, the spectrum is centered at 2.2 eV.

A much more direct and detailed comparison between the kinetics and temperature dependence of structural relaxation and the reduction in FEM variance is possible, and it leads to a very different conclusion. First, the heat release occurs over a wide temperature range and begins a few tens of degrees above room temperature. In fact, when care is taken to keep the as-implanted material at liquid-nitrogen temperature before beginning the calorimetry, a heat release can be observed at temperatures as low as −150 °C.[3] This in sharp contrast to the statement from Ref. 1, "only at a temperature above 450 °C can a difference in MRO be measured". Next, rather than comparing the activation energies, we can look at the time scale of the annealing process itself. At 500 °C, the heat release is over and done with in a matter of minutes,[2] yet the reduction in FEM variance persists for 5 h,[1] during which time no measurable heat evolves from the samples. From this direct comparison alone, it appears abundantly clear that the heat release is completely independent of real or perceived changes in MRO.

As a separate issue, it may be added that the kinetics of the heat release follow a bimolecular[2] rather then a simple exponential decay, which would indicate that fundamentally different processes are in operation. However, in Ref. 1, it is not shown, but rather assumed, that the process follows an exponential decay. Since the proposed MRO reduction would involve the disappearance of small crystallites, one would expect kinetics that accelerate as the grains get smaller (since grain *growth* is generally characterized by a square root of time dependence). The data shown in Fig. 2 of Ref. 1 did not show any accelerated kinetics, casting some doubt on the proposed interpretation in terms of MRO reduction.

In summary, the very different time and temperature dependencies of the heat release during structural relaxation of amorphous silicon and the reduction in variance measured by FEM show that the two processes are essentially unrelated, and that therefore the main conclusion of Ref. 1 cannot be valid.

[1] J.-Y. Cheng, J. M. Gibson, P. M. Baldo, and B. J. Kestel, J. Vac. Sci. Technol. A **20**, 1855 (2002).
[2] S. Roorda, W. C. Sinke, J. M. Poate, D. C. Jacobson, S. Dierker, B. S. Dennis, D. J. Eaglesham, F. Spaepen, and P. Fuoss, Phys. Rev. B **44**, 3702 (1991).
[3] S. Roorda, Nucl. Instrum. Methods Phys. Res. B **148**, 366 (1999).