

Reply to Comment of Professor T. Butz on “Oxidation of Hafnium and Diffusion of Hafnium Atoms in Hexagonal Close-Packed Hf; Microscopic Investigations by Perturbed Angular Correlations” by Chandi C. Dey, *Z. Naturforsch.* **67a, 633 (2012)**

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Prof. Butz in his comment basically argued that the fluctuation observed in hafnium metal after heating at 873 K for two days in air is due to oxygen atoms and not due to hafnium atoms as wrote in the paper. But I don't agree with his views on this point because of the two following arguments:

i) In fact, the relaxation effect arises due to fluctuation of atoms, ions or molecules near to the probe. From the fluctuating electric field gradient (EFG), one can determine directly the source of fluctuation. It is shown in the paper that the fluctuating quadrupole frequency matches quite well with the quadrupole frequency of hexagonal close-packed (hcp) hafnium. This point has been discussed in the text as

– ‘The quadrupole frequency corresponding to fluctuating EFG can be determined using the relation $\lambda_2^{\max} (\mu\text{s}^{-1}) \approx 3\omega_Q^f$ Mrad/s [18]. This has been found to be ≈ 53 Mrad/s for the value of $\lambda_2^{\max} = 160 \mu\text{s}^{-1}$ found at a temperature of 573 K. This value of ω_Q^f matches well with the value of quadrupole frequency of hcp hafnium (~ 50 Mrad/s) and supports again that spin relaxations observed at 873 K and lower temperatures are due to fluctuation of hafnium atoms’.

ii) It is shown that during initial heating of hafnium at 873 K, fluctuation also arises. But this time the static quadrupole frequency was found to be only due to hcp hafnium. If the fluctuation would be due to oxygen atoms as pointed out by Prof. Butz, a quadrupole frequency corresponding to HfO_{2-x} would be expected. However, no such quadrupole frequency was observed during initial heating at 873 K or during long time heating. This point was also clearly discussed in the text. The relevant portion of the text describes as – ‘The strong fluctuating signal can again be attributed to diffusion of hafnium atoms and hopping of oxygen can be ruled out as no signal due to oxygen deficient HfO_{2-x} is observed at reduced temperatures. The quadrupole frequency corresponding to HfO_{2-x} is expected to be closer to HfO_2 as found from earlier measurement [4]’.

It is shown that at room temperature and above, a weak frequency component ($\sim 10\%$) appears which is probably due to absorption of oxygen. But this does not change much with temperature. This point has been written in the text as – ‘Values of quadrupole frequency and asymmetry parameter for the weak component have been found to be $\omega_Q = 43.8(7)$ Mrad/s and $\eta = 0.65(3)$ with $\delta = 0$. This signal arises possibly due to trapping of oxygen atoms in the interstitial site of hafnium lattice [16]’. I think the absorption of oxygen in the interstitial site and fluctuation of hafnium at 873 K after heating for two days in air are two different phenomena.