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REPLY TO COMMENT

Reply to the comment on ‘Creation of P_b interface defects in thermal Si/SiO₂ through annealing’

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Abstract. Regarding the electron spin resonance work (Stesmans and Afanas'ev (1996) *J. Phys.: Condens. Matter* **8** L505) reporting on a newly resolved P_b interface defect generation mechanism operative during postoxidation annealing in inert ambient above $\sim 640^\circ\text{C}$, Stathis (*J. Phys.: Condens. Matter* **9** 3297) criticizes that no explanation has been offered for this finding *vis-à-vis* apparently deviating previous work. Additionally, it is insinuated that previous crucial P_b results have been obtained only after postoxidation annealing. We show these comments to be based on the overlooking of plain experimental facts.

In his comment [1] on our work [2] newly reporting a P_b defect creation process operative during postoxidation annealing (POA) at temperatures $T_{an} \gtrsim 640^\circ\text{C}$, Stathis raises various critical items propelled by the idea that ‘after vacuum annealing Stesmans’ results diverge’.

(i) In the first one, Stathis refers to a previous, seemingly identical work of his [3], in marked disagreement with our data, however. In particular, what is referred to in that work is figure 1, depicting for various (111) Si/SiO₂ structures the P_b density growth versus T_{an} by isochronal (2h) vacuum annealing, of which the present authors are well aware [4]. In that figure, there are indeed shown four data points in the range $T_{an} = 700\text{--}800^\circ\text{C}$, which, with allowance for experimental accuracy, do not show evidence for P_b creation. In one breath then is added that these data essentially confirm the ‘canonical’ picture inferred by Brower [5], criticizing us for not offering an explanation for our unexpected new finding.

Clearly, the latter concerns a disregard of repeatedly reported experimental facts and explanation [2,6]. As well stated in the cited works, the key underlying reason is an inadvertent incorrect monitoring of the P_b density in previous work. In his monumental work on the H- P_b interaction kinetics [5,7], Brower clearly stated, in a laudable scientific attitude, that he used the peak-to-peak height $2V_D$ of the derivative absorption signal rather than the prescribed double numerical integration (area under the absorption curve). This later proved incorrect due to dipolar-interaction-induced variation in both linewidth and shape with varying P_b density [8]—a natural effect. Brower also relied on the V_D method to cautiously verify the physical stability of the studied P_b entities (i.e., fixed P_b entity density, either passivated by H or not), reaching a positive conclusion from a POA experiment at 850°C for ~ 1 h, with no evident change in V_D . While this has ever since been cited as definite proof of the P_b bath thermal stability, it has obviously lost its grounds. Hence, with respect to Stathis’ work [3] in which it has explicitly been stated that $[P_b]$ was determined through correct double numerical integration, it is difficult to see how the four data points in [3] may be seen as ‘essentially a confirmation of Brower’s work’. The former argument has been well presented previously [2,6]; hence also, Stathis’ statement of ‘offering no

explanation of their new finding' *vis-à-vis* 'the canonical picture given by Brower' is not understood.

The conflicting four $[P_b]$ data points for $T_{an} \geq 700^\circ\text{C}$ in figure 1 of [3] remain not understood. Clearly, the failure to resolve the $[P_b]$ increase cannot have resulted from incorrect V_D monitoring. The likely explanation then is for it to have arisen from inadvertent inappropriate thermal sample processing. In a later comment, Stathis himself raises the possibility of an influence of the vacuum quality during POA, i.e., 3×10^{-6} ([1], Stathis) versus less than 4×10^{-7} torr ([2], Stesmans). The significance of that difference, however, is much doubted. In support, we have conducted POA experiments in both turbomolecular and diffusion-pump-generated vacuum, without noticeable difference in resulting $[P_b]$, however. The suggestion appears completely overturned by another observation of Stathis himself [9], reporting a P_b density of $2.4 \times 10^{12} \text{ cm}^{-2}$ in (111) Si/SiO₂ annealed at 700–800 °C for 2 h in a vacuum of $\leq 10^7$ torr.

(ii) In a next suggestion as to the 'discrepancy', Stathis alludes to the possible influence of dissimilar initial wafer cleaning. Specifically referred to is the use of an acetone rinse as the last step prior to oxidation, suggesting C contamination. This remark is deemed irrelevant. It ignores the previous report [10] that varying this last step (i.e., acetone rinse, dip in aqueous HF) does not affect the attained P_b density for equal thermal steps. In support, we add that our experiments described in [2] were repeated [11] on (111) Si/SiO₂ structures [12], fully processed in a technological facility without involvement of any organic chemical—with identical results, indeed.

(iii) Next, Stathis addresses the observation from the initial isochronal (~ 1 h, vacuum) depassivation behaviour of as-oxidized (dry) (111) Si/SiO₂ [2] that $[P_b]$ saturates toward $\sim 4.7 \times 10^{12} \text{ cm}^{-2}$, noting that this value closely corresponds to previously reported values for similar samples (see, e.g., [3], [10], [14] and [15]). For one, the value is indeed in striking agreement with the value $[P_b] = (4\text{--}5) \times 10^{12} \text{ cm}^{-2}$ reported for standard as-oxidized (111) Si/SiO₂ (*without any additional* POA step) over the whole range $T_{an} = 100\text{--}1000^\circ\text{C}$ [10]. Indeed, from an extended experiment [11], the value $N_0 = (4.9 \pm 0.4)$ is explicitly advanced as the naturally incorporated density of P_b sites during standard dry oxidation. However, as outlined above, this notion is incompatible with Stathis's statement that this value also agrees with his 'extensive experience' reporting a *maximum defect density* of $\sim 3 \times 10^{12} \text{ cm}^{-2}$ *after vacuum annealing* for T_{an} up to 800 °C [3].

(iv) It is tendentious to state that Stesmans has consistently reported P_b densities after vacuum annealing two to four times higher than reported by others. Clearly, taking the as-oxidized density as $\sim 4.7 \times 10^{12} \text{ cm}^{-2}$ (now apparently agreed upon) and comparing with the value consistently reported after vacuum annealing at $\sim 800^\circ\text{C}$ [2], scientifically correct is a factor of two. (For comparison, Brower generally reports a value of $(3\text{--}5) \times 10^{12} \text{ cm}^{-2}$ [14], with a stated absolute accuracy of a factor of two [16].)

(v) We can be brief about the comment stating that it is only after vacuum annealing that Stesmans' dipolar interaction effects are resolved, as well as 'unusual passivation behaviour'. This concerns a plain disregard of experimental facts. For one, it was well shown that dipolar effects, in terms of P_b linewidth and shape, are resolved from $[P_b] \sim 10^{11} \text{ cm}^{-2}$ onward on *as-oxidized* samples [8]. In the same spirit, little courtesy is involved in stating that dipolar effects have been unable to be observed by others [17]. As demonstrated, in terms of P_b linewidth and shape, it is simply necessary to measure the P_b signal under *spectroscopically correct* conditions as a function of $[P_b]$ to resolve these [8]. There are others, indeed, who do see effects [18].

Finally, as already mentioned in [11], we conclude by expressing agreement with the

general inference that the newly observed P_b generation effect may help clarify apparent discrepancies over various ESR works. Among other things, it explains how, for identical POA in vacuum at $\sim 800^\circ\text{C}$, P_b densities of $\sim 1 \times 10^{13} \text{ cm}^{-2}$ have consistently been reported by Stesmans, as noticed by Stathis. We now better understand previous ESR works on this matter. However this is as far as this conclusion can go. There is no excuse for interpreting this better understanding in the sense of attempting to nullify previous basic observations as artefacts from diverting interfaces as a result of thermal maltreatment. As to basic observations such as dipolar interaction effects in the P_b spectrum or improved H passivation data [6], when simply sticking to the experimental facts, the resolved creation effect is nowhere at the basis of these observations. On the contrary, it now puts them in clearer perspective. Negating experimental facts has proven to be a bad scientific guide in the past.

References

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- [4] The issue is addressed elsewhere (Stesmans A and Afanas'ev V V 1997 unpublished), but, obviously, some discussion is required here also.
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- [17] A discussion of why previous work has failed to resolve dipolar interaction effects was given elsewhere [8].
In retrospect, a main reason was that the observations were confined to the study of only *one* sample of *fixed* P_b density $\sim (3-5) \times 10^{12} \text{ cm}^{-2}$, that is, no measurements were carried out as *a function of* $[P_b]$.
- [18] See, e.g., Schoisswohl M, von Bardeleben H J, Bratus V and Mündler H 1995 *Thin Solid Films* **255** 163