Hydroxyl Groups on Germania Surfaces

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IT is well known that the properties of germanium junction devices are affected by reaction with gas, and there have been numerous studies in recent years dealing with the surface properties of germanium. However, the experimental emphasis has been on "clean" surfaces and on electronic

properties, and little attention seems to have been paid to the nature of the molecular species on germanium surfaces or, as is most likely in the case of practical devices, on oxidized surfaces or germania. We have found infrared techniques useful, and have observed the reaction of water vapour with germania to produce surface hydroxyl groups to occur at room temperature.

For example, trace A of the Figure shows the "background" spectrum of a germania powder having a surface area of 25 m^2/g. Spectrum B was recorded after the specimen had been exposed to water vapour at 5 torr for 15 min. There is a broad band centred near 3500 $cm.^{-1}$ typical of sorbed, hydrogen-bonded water, and a sharp peak near 3670 $cm.^{-1}$. The intensity of the sharp band increases after the specimen has been heated at 300° in water vapour (spectrum C). The sharp band is retained after the broad band is removed by pumping at 390° (spectrum D), but can itself be removed by pumping at 500°. The sharp band is in the O–H region, undergoes the characteristic isotopic shift when the surface is treated with D_2 or D_2O, is reversibly diminished in intensity and broadened when acetone or CCl_4 is adsorbed, and is consequently assigned to isolated hydroxyl groups on the germania surface.

The rate and extent of formation of the hydroxyl groups and, once formed, their existence on the surface, depend on a number of variables including the method of sample preparation, temperature, exposure to gases, and the like. Also, the hydroxyl groups appear to modify the reactivity of the surface with a variety of gases such as H_2O, CO, NH_3, or alcohols. Such effects are at present under study and will be reported in detail later. As surface reactions can influence the electronic properties of bulk materials, such effects are likely to be important in the study of practical junction devices.

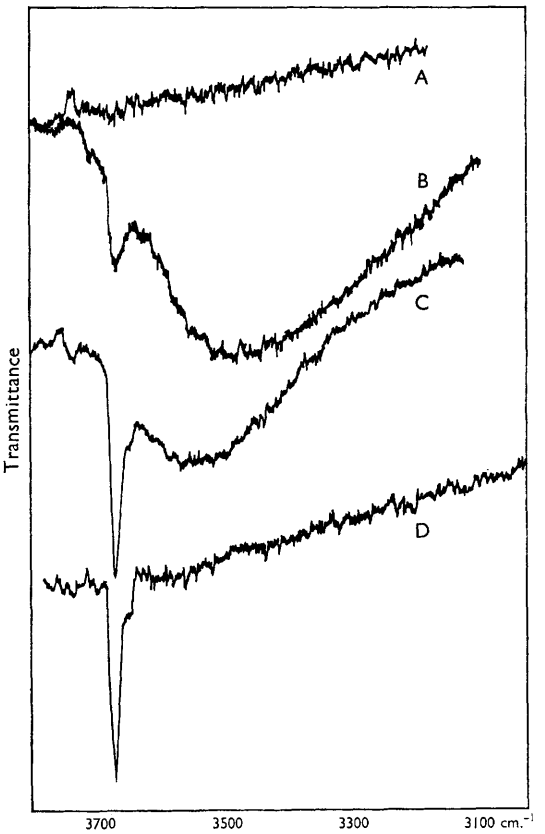

FIGURE. *Infrared spectra of surface* OH *groups.* A*: "background of a germania specimen.* B*: after exposure to water at* 5 *torr for* 15 *min. at room temperature.* C*: after heating in water vapour at* 5 *torr for* 1 *hr. at* 300° *and degassing at* 100° *for* 1 *hr.* D*: after degassing a specimen, treated as in* C*, for* 1 *hr. at* 390°. *The ordinates of spectra* C *and* D *are displaced to avoid overlap.*

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