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Combined XPD, STM, and LEED study of iron oxide films on Pt(111)

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The three complementary surface structure probes of x-ray photoelectron diffraction (XPD), scanning tunneling microscopy (STM), and low-energy electron diffraction (LEED) have been combined in a single instrument. This experimental system has been utilized to study the growth of iron oxide films on Pt(111) over thickness range from 0.75 to 3.0 monolayer(ML). Each film was formed by first depositing an overlayer of pure Fe with a certain coverage in ML and then thermally oxidizing the Fe at a temperature of 980K and in an oxygen pressure of $4x10^{-6}$ Torr. For films up to ~ 1 ML in thickness, a bilayer of Fe and O similar to those in bulk FeO parallel to a (111) plane is found to form. In agreement with a prior STM and LEED study by Galloway et al., we found this bilayer to be an incommensurate oxide film forming a lateral superlattice with short- and long- range periodicities of 3.1 Å and 26.0 Å. XPD, in addition, permits concluding that the topmost oxygen layer is highly relaxed inward by ~ 0.6 Å as compared to the bulk FeO(111) interlayer spacings, and that the stacking of the topmost O atoms with respect to the underlying Pt is dominated by one of two structurally very similar possibilities. It is further necessary to consider interactions over at least four atomic layers to explain this dominance of one stacking type. For thicker iron oxide films from 1.25 ML to 3.0 ML, the growth mode is essentially Stranski-Krastanov: iron oxide islands form on top of the FeO(111) bilayer mentioned above. For iron oxide films of 3.0 ML thickness, x-ray photoelectron spectroscopy(XPS) yields an Fe $2p_{3/2}$ binding energy and an Fe:O stoichiometry consistent with the presence of Fe_3O_4. XPD data further prove this overlayer to be Fe3O4(111)-magnetite in two almost equally populated domains with a 180° rotation between them. The structural parameters for this Fe_3O_4 overlayer generally agree with those of a previous LEED study, except that we do not find a terminating partial monolayer of Fe and arrive at a significant difference in the first Fe-O interplanar spacing. Overall, this work demonstrates the considerable benefits to be derived by using this set of complementary surface structure probes in such epitaxial growth studies.