Control of bonding and epitaxy at copper/sapphire interface

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The close-packed *c*-plane of sapphire, $(0001)_S$ ('S' denotes sapphire), has been widely used as a substrate for thin film growth. Metal/sapphire systems concerned, the interfacial bonding mechanism is greatly affected by the atomic structure and composition of the terminating plane of the $(0001)_S$ surface. The surface is not a cleavage plane and can be terminated in several ways (O-, single Al- or double Al-termination) due to the alternating stacking sequence of oxygen (O) and aluminum (Al) along the surface normal. *Ab initio* calculations of the surface energy predict the single Al-termination as the most stable surface configuration in dry vacuum and, indeed, UHV-cleaning routines consisting of high temperature annealing and Ar ion sputtering usually result in Al-rich $(0001)_S$ surface terminations. However, the O-terminated interface yields the highest work of separation for most of transition metals, implying the importance of the charge interaction between metal adatoms and oxygen ions at the interface. The O-terminated $(0001)_S$ surface, if assumed, however, is a highly unstable configuration because the lattice bonding of topmost oxygen ions is unsaturated, leaving surface dipoles. This termination can be stabilized if the topmost oxygen is partially evaporated, leaving oxygen vacancies, or completes the unsaturated bonding with foreign elements, especially hydrogen in the form of hydroxyl (OH). Recently, it has been shown by theoretical calculations and experimental characterizations that the $(0001)_S$ surface is readily hydroxylated upon being exposed to 1 Torr or more of H_2O. The surface OH groups formed by dissociative adsorption of water are known to modify the growth mode and wetting of metal films due to the surface chemical reactions between the OH and metal adatoms involving charge transfer. Residual hydrogen buried at the internal interface, however, is known to decrease the bonding strength and degrade the thermal stability of the deposited film. Obviously a hydrogen-free O-terminated interface will be best suited for making a robust and durable metal/ceramic interface. We report here the experimental methods to control the nature of bonding at copper/sapphire interfaces by utilizing various surface cleaning processes in ultrahigh vacuum (UHV), which can

interfaces by utilizing various surface cleaning processes in ultrahigh vacuum (UHV), which can tailor the termination of the $(0001)_S$ surface.

A clean hydroxylated surface [OH-$(0001)_S$] is obtained by room temperature oxygen plasma cleaning, on which Cu atoms adhere principally by polarization and with some characteristics of ionic bonding (Figure 1a and 2a). The surface can be sufficiently dehydroxylated by using Ar ion sputtering and annealing in UHV, resulting in an Al-rich surface, where Cu grows as a polycrystalline film and $CuAl_2$-type intermetallic Cu-Al bonding forms at the interface (Figure 1b). High temperature oxygen plasma treatment of the dehydroxylated surface can sufficiently oxidize the surface Al ions in a structure similar to γ-Al_2O_3 on which Cu_2O-type ionic-covalent Cu-O bonding can be activated to form at an elevated temperature after growth in a orientation relationship 30°-rotated from the close-packed directions of each crystal (Figure 1c and 2b). For the Cu film on the oxidized surface [O-$(0001)_S$], the thermal mismatch strain developing during thermal cycle is fully accounted by annihilation or generation of triangular networks of misfit dislocations along the $<1\bar{1}0>_{Cu}$ directions. We believe the plasma oxidation of the $(0001)_S$ surface is a promising route to modify the $(0001)_S$ surface into a polymorph of alumina, especially γ-Al_2O_3-like, resulting in the formation of strong copper/sapphire interface and this preparation method is applicable to other metal/sapphire systems.

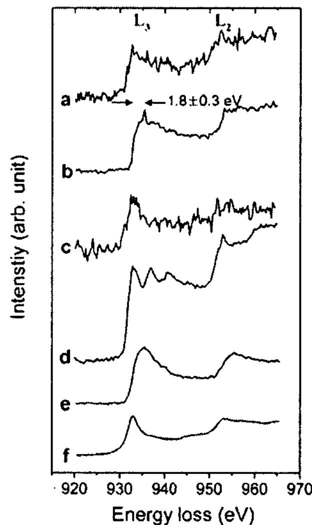

Fig. 1. Interface specific Cu-$L_{2,3}$ ELNES of the Cu films on the differently prepared $(0001)_S$ surfaces and the Cu-$L_{2,3}$ ELNES of the bulk Cu, $CuAl_2$ and Cu_2O. a, Cu/OH-$(0001)_S$ interface, b, Cu/Al-$(0001)_S$ interface and c, Cu/O-$(0001)_S$ interface. The spatial difference technique was applied to draw interface specific Cu-$L_{2,3}$ ELNES component at the interfaces by using STEM. d, Cu, e,

$CuAl_2$ and f, Cu_2O

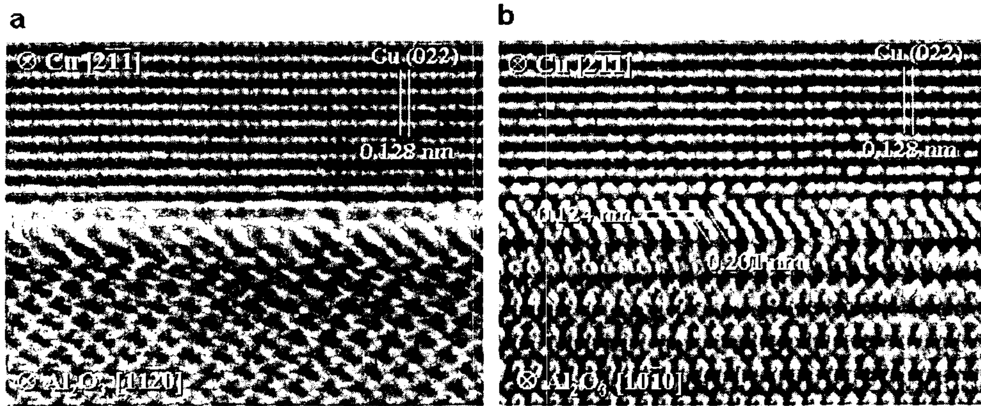

Fig. 2. HRTEM images of a, the Cu/OH-$(0001)_S$ and b, Cu/O-$(0001)_S$ interface.