Semiconducting chalcogenide buffer layer for oxide heteroepitaxy on Si(001)

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We report controlled laminar growth of a crystalline transition metal oxide on Si(001) *without* SiO_x or silicide formation by utilizing the chalcogenide semiconductor gallium sesquiselenide (Ga_2Se_3) as a non-reactive buffer layer. Initial nucleation of both pure and Co-doped anatase (TiO_2) is along Ga_2Se_3 nanowire structures, coalescing to a flat, multidomain film within two molecular layers. Arsenic-terminated Si(001) (Si(001):As) is stable against pure O_2, but oxidizes when both Ti and O_2 are present. The Si$-$$TiO_2$ valence band offset using either buffer layer is about 2.8 eV, producing a staggered band alignment.

Integration of crystalline oxides with silicon is a critical component of myriad proposed applications, including spin-electronic (spintronic),[1,2] ferroelectric and ferroic devices.[3] Anatase-structure TiO_2, which is nearly lattice matched to Si, shows particular promise for Si-based nanoelectronics[4] and, when doped with Co or Cr, spintronics.[5,6] However, full integration of new crystalline-oxide-based functionalities into Si technology is currently impeded by spontaneous formation of amorphous oxides and/or silicides at the Si/oxide interface.

Sub-nanometer buffer layers can prevent interface reactions while preserving oxide functionality. Most notable among current buffers is a Sr-O interlayer for $SrTiO_3$ heteroepitaxy on Si(001),[7,8] although substrate oxidation can occur during subsequent TiO_2 deposition.[9] Ultrathin SiO_2 has been utilized for TiO_2 growth, resulting in an amorphous titanium silicate interface layer.[10] An amorphous high band gap interlayer is acceptable for gate-insulator applications, but not for ferroelectric or ferromagnetic applications requiring crystalline oxides and/or non-scattering interfaces.

Here, we demonstrate a chalcogenide-based buffer layer, Ga_2Se_3/As, for laminar heteroepitaxy of both pure and cobalt-doped (5%) anatase (Co:TiO_2). Co:TiO_2 is known to be ferromagnetic at room temperature;[5,6] Ga_2Se_3 has a band gap of 2.1 eV,[11,12] between those of Si and TiO_2(1.1 eV and 3.2 eV, respectively), and nearly the same lattice constant.[13] Ga_2Se_3 forms a stable, epitaxial, non-reactive layer on Si(001):As.[14] The intrinsic vacancy structure of β-Ga_2Se_3, with one third of the cation sites vacant in a zinc-blende structure, also enables flexible strain relief. We observe neither oxide nor silicide formation at the buried Si interface, nor any buffer layer reactions; we also find a staggered band alignment, enabling electron transport from Si to TiO_2, but not vice versa. No evidence is found for the Co-rich surface clusters reported[9,15,16] with other growth methods. These features are extremely promising for possible Si-based spintronic applications of Co:TiO_2. We also investigated Si(001):As as a buffer layer; it is stable in pure O_2, but allows oxidation of Si in the presence of Ti.

TiO_2 and Co:TiO_2 films and the As and Ga_2Se_3 buffer layers were deposited on clean *p*-type Si(001) ($\rho = 0.02-0.1\ \Omega\cdot$ cm) by molecular beam epitaxy and characterized *in situ* by scanning tunneling microscopy (STM), photoemission spectroscopy (PES), and x-ray absorption near-edge structure (XANES). Buffer layers were deposited as by Ohta et al.,[14] first terminating the Si(001) surface with one monolayer of As and then adding $\sim$ 0.8 nm Ga_2Se_3. Pure Ti or a Co:Ti alloy rod (95% Ti, 5% Co) was heated with an electron beam in an oxygen background ($P_{O_2} = 5\times10^{-5}$ torr) to deposit TiO_2 or Co:TiO_2 at either room or elevated (350-400°C) temperature. XANES measurements showed films grown at either room temperature (RT) or 350°C to have a Ti L-edge structure consistent with anatase standards grown on $LaAlO_3$(001), and inconsistent with rutile. Higher temperature deposition (500-600°C) results in growth of

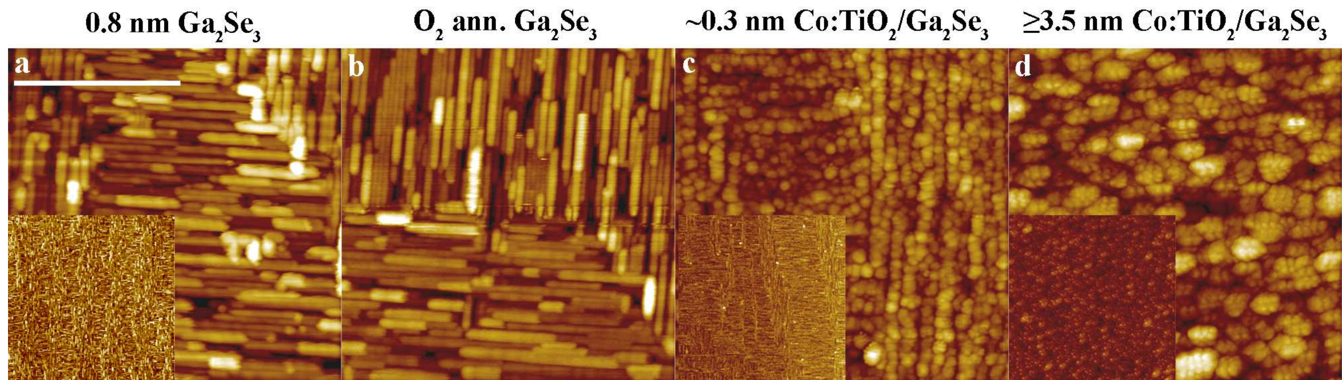

FIG. 1: **Surface morphology of buffer layers and oxide film.** (Color online) 100×100 nm^2 STM images (500×500 nm^2 insets): (a) ∼0.8 nm Ga_2Se_3; (b) O_2 (P_{O_2} ∼5×10^{-5} torr) annealed (T_{ann} = 450°C) Ga_2Se_3; (c) ∼0.3 nm Co:TiO_2 film on ∼0.8 nm Ga_2Se_3; (d) ≥3.5 nm Co:TiO_2 film on ∼0.8 nm Ga_2Se_3. Scale bar in (a) is 50 nm. Nanoridges are in [110] directions and differ in height by 0.27 nm. Image conditions: (a) 2.5 V, 0.07 nA, inset: -4.5V, 0.09 nA; (b) 2.8 V, 0.1 nA; (c) 2.8V, 0.09 nA, inset: 2.8V, 0.09 nA; (d) 2V, 0.12 nA, inset: 2.9V, 0.1 nA.

rutile nanocrystals; still higher destroys the buffer layer and oxidizes the substrate.[17]

The Ga_2Se_3 buffer layer self-assembles into oriented nanoridges, tens of nm long and 1-2 nm wide at their base [Fig. 1(a)], generated by ordered coalescence of intrinsic vacancies at the surface. The Ga-topped ridges have (111) Se facets forming the sides and change direction at each substrate step.[14,18] This morphology is stable against oxidation in a partial pressure of P_{O_2} = 5×10^{-5} torr at 450°C [compare Figs. 1(a) and (b)]. Photoemission spectroscopy shows no oxygen accumulation (within an experimental sensitivity of $\lesssim$ 2% of a monolayer). The observed narrowing, smoothing and aligning of the nanoridge morphology also occurs during an equivalent anneal without O_2 ($P_{tot} \leq 1\times10^{-10}$ torr). The root-mean-square (rms) surface roughness over 1.0 μm^2 is 0.24 nm, comparable to that of bare Si(001) (see Table I). On a smaller scale [Fig. 2(a), 30×50 nm^2], six nanoridge levels (0.27 nm height difference) are exposed on what was originally two Si terraces.

RT deposition of about 1 molecular layer (ML) Co:TiO_2 on this Ga_2Se_3/As buffer layer nucleates as 1 ML high clusters with centers spaced by 2-3 nm along the Ga_2Se_3 nanoridges [Fig. 1(c)]. The large-scale nanoridge morphology is unchanged (Fig. 1 insets). The first 1-2 ML have comparable roughness to the starting buffer layer (Table I). Deposition at 350°C [Fig. 2(c)] produces comparable morphologies, although the higher temperature (faster diffusion) growth leads to a larger spacing (3-4 nm) between the clusters. At coverages just below 1 ML, some underlying Ga_2Se_3 nanorods may be seen [*e.g.*, x= 14−18 nm in Fig. 2(f)-c], and sub-ML modulation is apparent on some larger surface islands.

Continued growth of Co:TiO_2 at either RT or 350°C results in laminar films without large surface clusters [inset, Fig. 1(d)]. At a thickness of ∼15-20 ML, the rms roughness of films grown at 350°C has increased by only ∼1/3 ML over the starting value (Table I); the film exhibits predominantly single ML height steps surrounding 5-10 nm diameter, kidney-bean shaped domains [Fig. 2(e)]. RT-deposited films are slightly rougher, exhibiting 7-10 nm diameter islands, 3-4 ML high [Figs. 2(d) and 1(d)].

Bright dots of apparent height 0.1 nm, spaced by $\sim 4-6$ surface unit cells, are seen in the positive tip bias, filled-state images of T_{dep} = 350°C Co:TiO_2 films [Fig. 2(e)]. Although we cannot rule out Co clustering, their spacing matches the expected distance between uniformly distributed Co atoms, which comprised 5% of the source metal. Similar bright spots, though with higher density and concentrated at step edges, were reported for STM of Co:TiO_2 films on $SrTiO_3$,[19] where they were attributed to isolated Co atoms that remained after clusters dissolved upon annealing. In bulk Co:TiO_2, Co^{2+} substitution for Ti^{4+} likely has an associated oxygen vacancy; a bright spot in occupied state images (presumably dominated by O 2p emission) indicates enhanced negative charge, consistent with an intact O lattice near a surface Co^{2+} impurity. The local morphology of pure TiO_2 films (not shown) is indistinguishable from Co:TiO_2 except for these bright dots.

Chemical reactions at the buried Si-buffer layer inter-

TABLE I: **Z-range RMS roughness (nm) as a function of preparation and scan size.** For anatase films, Co:TiO_2 values in roman, TiO_2 in *italics*; deposition at RT, with T_{dep} = 350°C in parentheses.

Scan Range (μm^2)	Bare Si(001)	Si(001):As	∼0.8 nm Ga_2Se_3	∼0.3 nm Co:TiO_2 *TiO_2*	≥3.5 nm Co:TiO_2 *TiO_2*
1.0×1.0	0.26	0.14	0.24	0.21	0.32
0.5×0.5	0.19	0.10	0.23	0.27 (0.29) *0.29 (0.28)*	0.36 *0.40 (0.34)*
0.1×0.1	0.06	0.07	0.29	0.28 (0.24) *0.28 (0.26)*	0.35 *0.43 (0.35)*

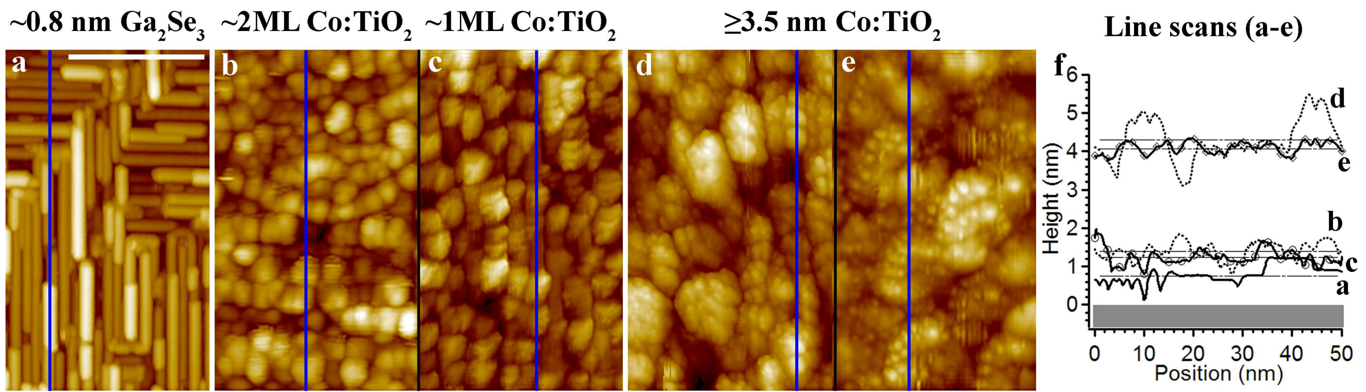

FIG. 2: **High resolution surface morphology of buffer layer and oxide films.** (Color online) 30×50 nm^2 STM images of: (a) ∼0.8 nm Ga_2Se_3; (b-e) Co:TiO_2 films on ∼0.8 nm Ga_2Se_3: (b)∼0.2 nm (2 ML), T_{dep} = RT; (c) ∼0.08 nm (1 ML), T_{dep} = 350°C; (d) ≥3.5 nm (20 ML), T_{dep} = RT; (e) ≥3.5 nm (20 ML), T_{dep} = 350°C; (f) cross-sectional line scans [110] (vertical lines) from (a-e). (a) solid line, (b) dotted line, (c) solid+circles, (d) dotted line, (e) solid+diamonds. Scale bar in (a) is 20 nm. Image conditions: (a) -5.4V V, 0.09 nA; (b-c) 2.8 V, 0.09 nA; (d) 1.8V, 0.09 nA (e) 3.6 V, 0.1 nA.

face were investigated with photoemission spectroscopy (PES) at the Advanced Light Source in Berkeley, CA (Beamline 7.0.1) (Fig. 3). Both Si(001):As and Ga_2Se_3 buffer layers are inert in partial pressures of O_2 (P_{O_2} = 5×10^{-5} torr) and $T_{ann} \leq 500$°C. High resolution, surface-sensitive, core-level spectroscopy (Fig. 3) reveals no oxidized Si component for either Ga_2Se_3 or Si(001):As. In the presence of both Ti and O_2, a significant oxidized Si 2p component is observed for Si(001):As (peak at 102 eV in Fig. 3), indicating Ti catalyzes the Si−O reaction. The As 3d (not shown) also shows a reacted component upon TiO_2 deposition. TiO_2 growth on Ga_2Se_3/Si(001):As, however, shows no reacted substrate components. As the TiO_2 film grows thicker, the Si 2p peak neither shifts in energy nor shows any additional components; likewise the Ga 3d, As 3d, and Se 3d emission (not shown). All substrate peaks attenuate exponentially, as expected for a non-reactive, laminar deposition.[17]

We propose the TiO_2 nuclei react with the Se-terminated sides or valleys between the nanoridges. Ga−Ti interactions would lead to metallic states in PES, while Ga−O reactions would cause a new Ga 3d component; neither were observed. Interface Ti−Se interactions, on the other hand, may not have a clear PES signature. Se atoms with non-bonded lone pair orbitals can effectively "oxidize" the Ti adatoms and stabilize them at the surface for reaction with incident O_2. No O adsorbs without Ti present. For Si(001):As, we suggest that Ti rests in the trenches between the As dimer rows, weakening the Si−As bonds to promote Si oxidation. The larger bond enthalpy of Si−O relative to Ti−O leads to preferential bonding to Si.

A key parameter for possible electronic device applications of TiO_2/Si is the band alignment. Fig. 3 shows valence band emission, highlighted with lines marking the band edges, using the known energy difference[20] between our measured Si 2p or Ti 3p emission and the respective

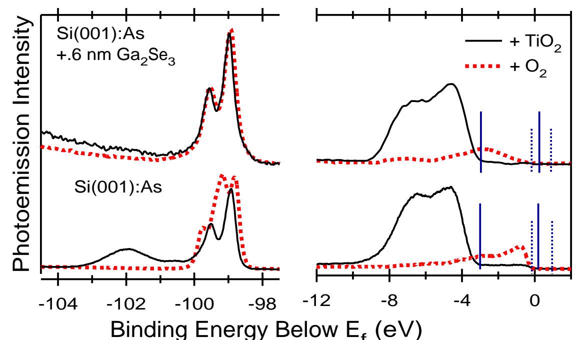

FIG. 3: **Chemical passivity of buffer layer.** (color online) Si 2p (left) and valence band (right) normal emission photoelectron spectra for Si(001):As (bottom) and Si(001):As + 0.6 nm Ga_2Se_3(top) plus O_2 (dotted curve) or ∼0.5 nm TiO_2 film (solid curve). Photon energy, $h\nu$= 160 eV. Si 2p peak intensities scaled to same area. Vertical lines show location of VBM and CBM for TiO_2 (solid) and Si (dotted) (see text).

VBM, and band gaps of 3.2 eV for anatase and 1.1 eV for Si. The valence band offset (VBO) is 2.77 ± 0.1 eV for the Ga_2Se_3 buffer layer and 2.86 ± 0.1 eV for As alone. These are well above the VBO values of 1.65−2.55 eV for TiO_2 on a SiO_2 buffer layer,[10] 1.93 eV for SrO/$SrTiO_2$ buffers,[20] and 2.0 eV predicted from alignment of charge neutrality levels.[21] This indicates a significant interface dipole contribution from the As and Ga_2Se_3 buffer layers, possibly including As interdiffusion into the Ga_2Se_3 film. It should therefore be possible to shift this alignment through manipulation of interface dipoles in the Ga_2Se_3 film. Our measured VBO identifies a staggered band alignment, with the anatase CBM about 0.7 eV below of that of Si; this allows electron transport from Si to TiO_2, but forms a barrier in the other direction.

In summary, we presented heteroepitaxy of laminar

TiO_2 and Co:TiO_2 on Si(001) without reactions at the buried silicon interface through use of Ga_2Se_3 as a buffer layer. The oxide nucleates between Ga_2Se_3 nanoridges, with further growth leading to laminar films with low surface roughness. No segregated particles are observed. We do not find successful oxide heteroepitaxy on As-terminated silicon. Finally, we find a staggered band alignment between the TiO_2 film and the Si substrate. We believe Ga_2Se_3 films may be extended for use as a buffer layer with other oxide heteroepitaxial systems.

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