Absolute determination of film thickness from photoemission: Application to atomically uniform films of Pb on Si

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We report on a method to unequivocally determine the thickness of a film in terms of atomic layers, as demonstrated by a study of Pb growth on Si(111). Deposition at low temperatures on a pretreated Si substrate results in atomically uniform Pb films. These films exhibit large monolayer-by-monolayer variations in electronic structure as observed by angle-resolved photoemission. Intense and sharp peaks derived from quantum-well states are observed for odd film thicknesses $N=5$, 7, and 9 monolayers, but not for the adjacent even film thicknesses $N=4$, 6, 8, and 10 monolayers. The dramatic differences facilitate an accurate calibration of the amount of Pb deposited. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1783019]

The continued miniaturization of Si-based electronic devices is pushing component layer thicknesses toward the nanoscale. A critical hurdle along this path is atomistic fluctuation. Such thin films can suffer substantial property changes if the layer thickness is changed by just one atomic layer or if there is roughness at the monolayer level. The effect is generally on the order of $1/N$, where N is the thickness of the film in terms of monolayers (ML). At the nanoscale, $1/N$ can be as large as 20%, and the consequences can be severe or even catastrophic for device performance. Exact control of layer thickness or atomic uniformity is thus a critical issue. In this work, we show that Pb deposition on Si(111) at 100 K can lead to atomically uniform thin films provided that the Si substrate is pretreated appropriately and we describe a technique to precisely determine the thickness of a film. The resulting films support quantum-well states due to electron confinement by the band gap in the Si substrate and the Pb-vacuum barrier.[1–3] A measurement of such states by angle-resolved photoemission reveals a quantum electronic structure that varies substantially as the film thickness undergoes monolayer increments and exactly determines the film thickness.

Our angle-resolved photoemission data was taken at the Synchrotron Radiation Center in Stoughton, Wisconsin, with a normal-emission geometry using a Scienta analyzer. The Pb films were prepared by sequential incremental deposition. Three major peaks, at binding energies of 0.40, 0.26, and 0.15 eV below the Fermi level, attain their maximum intensities at film thicknesses of $N=5$, 7, and 9, respectively, while no such peaks are observed at the even layer thicknesses of $N=6$ and 8 in the same energy range. Selected spectra for coverages from $N=5$ to 7 are shown in Fig. 1 to illustrate the dramatic variations in spectral lineshape. These peaks represent quantum-well states formed by confinement of the Pb p-band electrons by the Si band gap on the substrate side and the Pb-vacuum barrier on the vacuum side. No such quantum-well states exist for $N=6$ and 8, as will be explained below.

As seen in Fig. 1, the intensity of the quantum-well peak that is a maximum at $N=5$ diminishes as the film thickness increases from 5.0 through 5.3, 5.5, and 5.8. At $N=6.0$, this peak disappears, leaving behind a spectrum with little emission intensity. Further increasing the film thickness brings out a peak at a somewhat lower binding energy, which maximizes at $N=7$. The fact that the $N=6$ spectrum shows little emission at positions corresponding to the $N=5$ and 7 peaks indicates that the film thickness is uniformly 6 ML. Any significant mixture of $N=5$ and 7 patches or domains would have given rise to peaks at those positions. The continued reduction of the $N=5$ peak for thicknesses between $N=5$ and 6 simply means that the area covered by 5 ML is decreasing, while the area covered by 6 ML is increasing. Likewise, the continued increase of the $N=7$ peak for film thicknesses beyond $N=6$ through 7 reflects the continued increase of the portion of surface area covered by 7 ML at the expense of the area covered by 6 ML. These results establish that the films are atomically uniform to within a few percent when the coverages equal integer numbers of monolayers.

The appearance of intense peaks for odd N results from the interplay of the Pb band structure and the Si band gap. From data taken over a wide thickness range, it is concluded
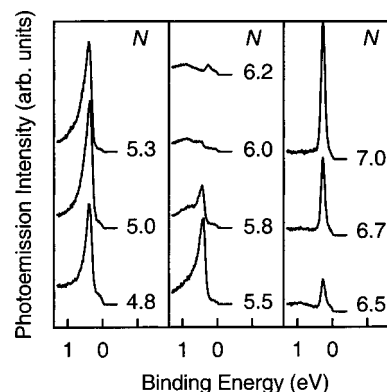

FIG. 1. The line scans show the photoemission intensity as a function of binding energy relative to the Fermi level for various Pb coverages N in terms of monolayers. Quantum-well peaks are fully developed at $N=5$ and 7.

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that the lower edge of the Si band gap (1.12 eV) lies at 0.5 eV below the Fermi level. Therefore, electrons in the Pb film with binding energies within 0.5 eV of the Fermi level are confined, giving rise to sharp and intense quantum-well peaks. Electrons at higher binding energies are not confined. Nevertheless, partial reflection at the Pb–Si boundary can give rise to resonances which appear in photoemission as weak and broad peaks. Further evidence for the confinement edge at 0.5 eV is seen in the line scan of the peak at $N=5$ in Fig. 1. This peak, with a binding energy very close to the confinement edge, is asymmetric. Its higher binding energy side is substantially broader because this portion of the spectral weight lies outside of the confinement range. A detailed examination of the peaks at various thicknesses establishes that the confinement edge is at 0.5 eV below the Fermi level. From this, the Schottky barrier height is calculated to be about 0.6 eV.[4,5] First-principle calculations of quantum-well states have been performed for freestanding Pb films.[5] The results are in close agreement with our measured peak positions if the theoretical values are lowered by 0.2–0.3 eV. These small differences can be attributed to boundary effects caused by a phase shift introduced by the Pb–Si interface.[2] The same analysis shows that within the 0.5 eV confinement range, no quantum well states are expected for $N=6$ and 8; in agreement with the observation.[4,6]

Numerous groups have experimented with Pb growth on Si, mostly by direct deposition on the (7×7) reconstructed Si(111) at various temperatures.[6–11] The resulting films were inevitably rough, exhibiting no atomic-layer resolution, as verified by our extensive, but futile, effort in making a smooth film. In the present experiment, the atomic-layer uniformity is achieved by first depositing close to 2 ML of Pb on Si(111)-(7×7). The sample is then annealed at a temperature above 400 °C, and the Pb desorbs gradually as verified by photoemission measurements of the Pb $5d$ and Si $2p$ core-level intensities.[12] The desorption curve exhibits breaks that correspond to the formation of distinct phases.[10,12,13] The α phase forms at a residual Pb coverage of 1.1 ML (equivalent to 4/3 ML of Si coverage). Its structure is a somewhat compressed full ML of Pb sitting on a bulk-truncated Si(111). The β phase forms at a residual Pb coverage of 0.28 ML (equivalent to 1/3 ML of Si coverage). Its structure is a bulk-terminated Si(111) decorated by Pb adatoms arranged in a $(\sqrt{3}\times\sqrt{3})R30°$ configuration to minimize the number of dangling bonds. Our experiment shows that deposition of Pb on the α phase, the β phase, or any intermediate phases at a low temperature (100 K) leads to atomically uniform films. The final results are the same for the same total amounts of Pb deposition including the initial Pb coverages.

The data set shown in Fig. 1 was taken from films grown on an α phase substrate. The intensities of the $N=5$, 7, and 9 major quantum-well peaks (Fig. 1) are measured as a function of time of Pb deposition (top panel in Fig. 2). They peak at Pb coverages of 4, 6, and 8 ML, respectively, on top of the α phase based on readings from a thickness monitor. Accounting for the Pb monolayer already present on the α phase, the total Pb thicknesses are then 5, 7, and 9 ML, respectively. The layer-by-layer variation allows us to take the difference in coverage between the first and the last peaks in Fig. 2 to be exactly 4 ML. This establishes an absolute thickness calibration, and the resulting thickness scale is shown at the top of the figure. This procedure shows that our
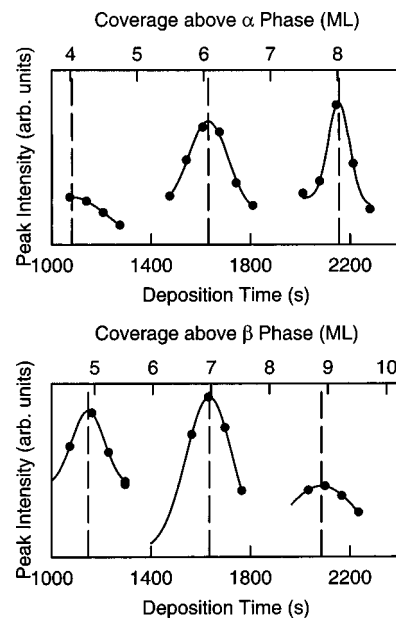

FIG. 2. Major quantum-well peak intensities measured as a function Pb deposition time above an α phase substrate (top panel) and a β phase substrate (bottom panel). The vertical dashed lines indicate positions of maximum intensities, which should correspond to completed atomic layers. In each case, the first peak and the last peak should differ in coverage by 4 ML, which establishes the absolute thickness scale shown on top of each panel. The difference in coverage between the two cases by almost 1 ML is accounted for by the difference in initial Pb coverage between the α and β phases.

thickness monitor was off by 5%. The bottom panel shows a similar analysis for data taken from films deposited on a β phase substrate. The intensities of the major quantum-well peaks attain their maxima at Pb coverages slightly less than $N=5$, 7, and 9, or almost 1 ML more than the corresponding cases for deposition on the α phase. This is consistent with the calculation that it takes $1.11-0.28=0.83$ ML to convert the β phase to an α phase with a fully populated first ML. Additional data at intermediate coverages are also consistent.

Why does Pb pretreatment promote uniform film formation, while direct deposition on Si(111)-(7×7) does not work? A possible explanation is that the (7×7) surface, with its complicated reconstruction involving adatoms, dimers, corner holes, and a partial stacking fault, is not smooth on the atomic scale. These structural features can pin the Pb growth locally at low temperatures, resulting in small crystallites that are structurally incoherent. Increasing the substrate temperature to promote long-range diffusion and structural coherence leads to formation of islands instead of smooth films due to electronic effects.[8,14] Pretreatment of Si by Pb leads to a smooth bulk-terminated Si substrate with a well-ordered Pb overlayer. This can be a good template for smooth growth upon further deposition at low temperatures. Our results illustrate an important issue in film growth—the initial surface structure can be a deciding factor for the morphological development of films. As shown in this study, proper conditioning of the starting surface allows us to make uniform metallic films on Si, a result of potential interest and importance for Si-based nano- and quantum electronics.

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