Articles

Growth and Reactivity of CuCl on Si(111)

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Films of cuprous chloride (CuCl), a zinc blende semiconductor lattice matched to Si, were deposited by molecular beam epitaxy onto a room-temperature Si(111)(7 × 7) substrate and studied with surface-sensitive spectroscopies. Low-energy electron diffraction revealed an ordered 1 × 1 pattern at several monolayers of coverage, and Auger electron spectroscopy yielded an approximate Cu to Cl surface stoichiometry of one-to-one for as-deposited films. Ion scattering experiments indicated that the initial stage of CuCl growth involved Cl–Si bonding. Annealing the films initiated chemical reactions, which resulted in the loss of Cl and the formation of a Cu silicide.

Introduction

Cuprous chloride (CuCl) is a I–VII zinc blende semiconductor with a wide bandgap (3.4 eV), which is the result of the ionicity of the chemical boding between Cu and Cl. Epitaxial overlayers of CuCl on Si represent an extreme in heterostructure interfaces, in terms of having a highly ionic overlayer on a strictly covalent substrate. Structurally, Si is an ideal template for CuCl growth since the lattice mismatch between CuCl (5.42 Å) and Si (5.43 Å) is less than 0.2%. The binary semiconductors (primarily III–V compounds) grown on Si to date have had varying degrees of ionic character, but most have had neither a lattice parameter close to Si nor strongly ionic bonding character.

A previous report claimed the epitaxial growth of CuCl on Si(111), although the details of the growth technique were not revealed.[1] The films grown for that investigation were of a bulk nature (50–500 nm) and had atmospheric stabilities for periods greater than 6 months. The resultant CuCl/Si interface structures were reported to exhibit ideal diamagnetic and paramagnetic responses that were attributed to mechanisms responsible for high-temperature superconductivity.[1]

Bulk thermodynamic considerations indicate that the CuCl/Si interface should be chemically unstable with respect to copper silicides and chlorosilanes. The enthalpy of reaction for

$$4\mathrm{CuCl(s)} + \mathrm{Si(s)} \rightarrow 4\mathrm{Cu(s)} + \mathrm{SiCl_4(g)} \qquad (1)$$

is calculated to be −27 kcal from standard tabulated enthalpies of formation.[2] It is also important to recognize that surfaces under ultrahigh-vacuum (UHV) conditions are open systems, and any reaction that forms gas-phase products is favored by entropic considerations. Even in a closed system, CuCl and Si have been observed to react for temperatures less than 350 °C by powder diffractometry.[3] Experimental results from a recent thermal desorption study[4] of chlorine on Si(111) demonstrate that $SiCl_4$(g) can be formed and desorbed at temperatures near 300 °C, which also supports the spontaneity of the reaction as written in eq 1.

The initial growth of CuCl on Si(111) may be compared to the heteroepitaxy of another metal–halogen compound, CaF_2. Bulk enthalpic calculations show that CaF_2 and Si should not react. However, studies of the electronic structure and atomic geometries of the CaF_2/Si interface show that a chemical process, the loss of one equivalent of F coupled with subsequent Ca-Si bond formation, occurs in the first monolayer of the CaF_2 film.[5,6] Further epitaxy takes place with complete CaF_2 units. The nature of the desorbing fluorine species is unknown. At high annealing temperatures (800 °C), experiments have shown that the CaF_2/Si system becomes entropically unstable and yields a Ca–silicide layer accompanied by loss of all fluorine.[7]

In this study, CuCl films were grown on Si(111) substrates by molecular beam epitaxy (MBE). The primary methods of characterizing the CuCl/Si interface were low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and several variants of low-energy ion scattering (LEIS), which were used to determine the stoichiometry and local atomic arrangements on the surfaces of the deposited and annealed films. The primary LEIS technique employed was impact-collision ion scattering spectroscopy (ICISS), in which the scattering angle is fixed near 180° to simplify the interpretation of the scattering ion angular distributions.[8] The films were then annealed in UHV and characterized again to determine if the films would evolve in structure or react chemically with the Si substrate.

Experimental Procedure

The CuCl evaporation and the subsequent characterization were carried out in a UHV chamber (base pressure below 2×10^{-10} Torr)

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that has been previously described, except for the addition of a new Coloutron ion source.[9] The Si(111) substrate surface was prepared by annealing the sample to 1050 °C, as measured with an optical pyrometer, which yielded a sharp 7 × 7 LEED pattern with a carbon contamination level of less than 1% as determined by AES. The CuCl epilayers were grown from a quartz Knudsen cell operating at 390 °C (±10 °C) for a deposition rate of approximately 1 Å/min as determined by a quartz crystal oscillator. The background pressure was less than 10^{-9} Torr. Since CuCl sublimes congruently, the stoichiometry of the deposited film should be one-to-one unless there is a chemical reaction or adsorbate decomposition at the Si surface. The sticking probability of CuCl on Si surfaces is not known, but it is assumed to be nearly unity on a room-temperature substrate. One- to one-hundred-monolayer (ML) coverages of CuCl were grown directly on the room-temperature Si(111)(7×7) substrates. AES characterizations were performed with standard Varian four-grid retarding field analyzer (RFA) optics with a 2.5-keV primary electron beam, and the Auger response was corrected for the RFA electron transmission characteristics. Auger sensitivity factors were determined relative to those in ref 10, resulting in the following relative sensitivity factors: Cl (181 eV), 7.62; Cu (920 eV), 0.23; Si (92 eV), 3.4. The exposure of the grown films to the electron beam was minimized since CuCl is known to be electron-beam sensitive. Postdeposition anneals were performed by resistively heating the Si substrate with the temperature determined by an infrared pyrometer.

The LEED patterns of the Si(111)(7×7) substrates were used to evaluate the quality of the surface template and to align the azimuths for the various ion-scattering experiments. The LEIS energy scans were performed initially with both 5-keV He^+ and Li^+ projectiles incident along various azimuths. The backscattered ions were detected with an electrostatic analyzer, which was fixed at 155° for most of this investigation. The ICISS studies were performed using 5-keV Li^+, and the detector fixed at a constant 155° scattering angle. For these scans, the electrostatic analyzer was set to the kinetic energy corresponding to elastically scattered ions in the LEIS energy scans for Cu, and the scattered ion intensity was measured as a function of polar angle between the incident ion beam direction and the surface plane.

Results and Discussion

The depositions of 1–100 ML of CuCl on the Si(111) produced diffuse 1×1 LEED patterns, and AES measurements indicated an interface stoichiometry for Cu/Cl of 1:1 within experimental error. LEIS energy scans employing 5-keV Li^+ and He^+ revealed a significant enhancement of the Cu scattering signal from that expected for stoichiometric CuCl. The absolute cross sections for LEIS are not determined accurately, but a relative surface atomic composition within several percent is determined easily under normal experimental conditions. Energy scans with incident 5-keV He^+ yielded a much different apparent interface stoichiometry than did the Li^+ scans. The features in the Li^+ spectra were highly reproducible, whereas the features in the He^+ scans were not. Comparison of He^+ and Li^+ energy scan spectra indicated severe differential neutralization effects associated with the path-dependent neutralization of the He^+. A comparison of respective Li^+ and He^+ energy spectra for 1 ML of CuCl on the Si substrate is presented in Figure 1.

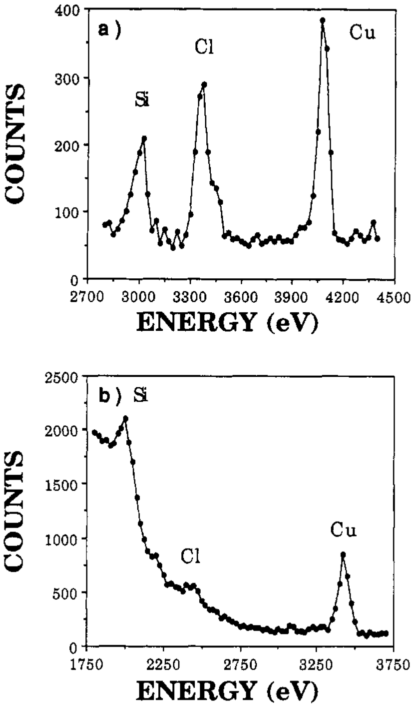

Figure 1. Comparison of energy scans from 5-keV (a) He^+ and (b) Li^+ backscattered from a 1-ML CuCl coverage on Si(111). The ion beam was normal to the surface plane with the detector set at 155°. The ratios of the differential cross sections for He^+ and Li^+ projectiles on the various target atoms are nearly the same. The difference in the relative peak areas are the result of neutralization effects.

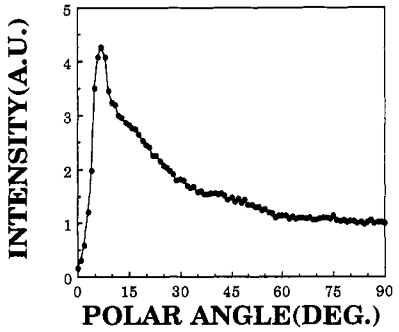

Figure 2. Experimental ICISS polar scan for 5-keV Li^+ scattered at 155° from the Cu atoms of a 1-ML CuCl overlayer on Si(111) along the Si[1$\bar{1}$0] azimuth. The surface flux peak (SFP) is sharp, and the lack of shadowing and blocking features at angles larger than the SFP indicates that the epilayer is Cu-terminated with a large interatomic distance. The experimental intensities were normalized at the polar angle of 90°, at which there should be no interatomic flux enhancement.

An ICISS polar scan for 5-keV Li^+ scattering from the Cu atoms of a nominal 1-ML CuCl epilayer is shown in Figure 2. There is an intense surface flux peak (SFP) at low polar angle with no intensity modulations at larger polar angles. This shows that Cu terminates the CuCl/Si interface and suggests Cl–Si bonding at the interface. The appearance of the SFP at such a low angle is indicative of a large interatomic distance between top-layer Cu atoms. ICISS scans were performed along several different crystal azimuths to ensure that Cu atoms comprised the top-layer atoms along all crystallographic axes. No experimental data were taken with Cl as the specific ICISS target atom because of the large background that can be seen in the Li^+ energy spectrum of Figure 1. Without more information about the underlying Cl structure, no quantitative model of the CuCl overlayer could be determined other than the certainty that Cu occupies the outermost layer of the film. For thin layers of GaAs on Si(111), the As anion is observed to be bound to the Si,[11] which is consistent with the Cl–Si bonding postulated above. However,

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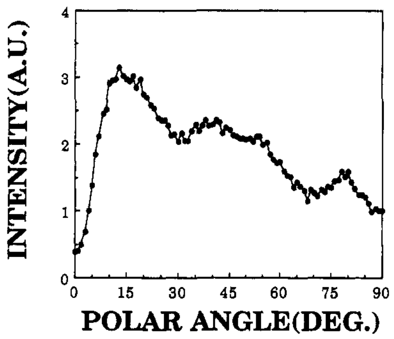

Figure 3. Experimental ICISS angular distribution from 5-keV Li$^+$ scattered from the Cu atoms along the Si$[1\bar{1}0]$ azimuth of the copper silicide 5×5 structure that results from annealing the 50-ML CuCl film on Si(111) to 550 °C. The SFP is at a low angle and is extremely wide, indicating that there is more than one type of exposed Cu atom. The Cu–Cu shadow cones are apparent at angles larger than the SFP as relative minima in the scan. The shadowing features are representative of scattering events from subsurface Cu atoms. The experimental yields were normalized at 90°.

the GaAs and CuCl on Si interfaces have significant differences, since CuCl is deposited stoichiometrically, whereas GaAs is thought to have an extra As layer at the interface and to form an As–Ga–As layer on Si(111).[11]

After low-temperature (300 °C) postgrowth anneals of samples with 50 ML of CuCl, the CuCl/Si system displayed a faint hexagonal 5×5 LEED pattern, and AES characterization revealed a major loss of Cl from the film. The Cl from the film was removed entirely by annealing to temperatures over 350 °C, but the Cu remained. The Cu/Si 5×5 LEED pattern sharpened upon annealing to 550 °C. The hexagonal 5×5 LEED pattern of a Cu/Si(111) surface has been identified as copper silicide on Si(111) by several previous investigators.[12,13] It was possible, by flashing the substrate to 1050 °C, to remove all traces of the copper–silicide epilayer and recover a pristine Si(111).

Both AES and LEIS spectra were collected from the Cu/Si 5×5 structure, and only Cu and Si were found. The ICISS scan of the Cu/Si 5×5 surface is totally different from the 1×1 CuCl/Si interface, as shown in Figure 3. The differences in the backscattered ion intensities are especially apparent at high polar angles, where strong blocking and shadowing features are evident. The polar scan in Figure 3 reveals that there are at least two inequivalent Cu sites exposed to the ion beam. The intensity of the SFP shows that Cu atoms are the outermost on the surface, but the width of the peak, especially compared to the SFP of Figure 2, indicates that there may be more than one type of outermost Cu site. The intensity minima at higher polar angle reveal that subsurface Cu is shadowed by either Cu or Si atoms, which is characteristic of a many-layer-thick copper silicide film.

The observed chemical reactions between CuCl and Si should not be surprising, since Cu is routinely used as a catalyst for the large-scale synthesis of chlorosilanes from methyl chloride and solid silicon.[14] One view is that Cu combines with the methyl chloride to form CuCl and a short-lived Cu–methyl compound. The latter dissociates into a methyl radical, which disrupts the Si lattice. This reduction reaction transfers a Cl to a Si at the expense of a Si–Si bond. Thus, for the observed reaction between CuCl and Si, the Cl is most likely removed from the system as a volatile chlorosilane. Give the facile nature of the reaction, the anomalous electrical and magnetic properties attributed to CuCl in ref 1 were most likely the result of a reacted CuCl/Si interface.

Conclusions

The growth of CuCl on a room-temperature Si(111) substrate forms a stoichiometric overlayer with a 1×1 LEED pattern. In situ ICISS experiments show that Cu forms the outermost layer of the CuCl film, which implies Cl–Si bonding at the Si interface. This contrasts to the Ca–Si bonding observed for CaF_2 on Si(111). AES, LEED, and LEIS all indicate that a chemical reaction takes place at the CuCl/Si(111) interface at temperatures as low as 300 °C, liberating Cl and resulting in a copper silicide thin film. Since the CuCl–Si interface is so reactive, a lattice-matched template other than Si should be used to grow epitaxial CuCl films.

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Registry No. CuCl, 7758-89-6; copper silicide, 12643-20-8.

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