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Encapsulation of the heteroepitaxial growth of wide band gap γ-CuCl on silicon substrates

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Abstract

γ-CuCl semiconductor material has been identified as a candidate material for the fabrication of blue-UV optoelectronic devices on Si substrates due to its outstanding electronic, lattice and optical properties. However, CuCl thin films oxidise completely into oxyhalides of Cu II within a few days of exposure to air. Conventional encapsulation of thin γ-CuCl by sealed glass at a deposition/curing temperature greater than $250\,°C$ cannot be used because CuCl interacts chemically with Si substrates when heated above that temperature. In this study we have investigated the behaviour of three candidate dielectric materials for use as protective layers for the heteroepitaxial growth of γ-CuCl on Si substrates: SiO_2 deposited by plasma-enhanced chemical vapour deposition (PECVD), organic polysilsesquioxane-based spin on glass material (PSSQ) and cyclo olefin copolymer (COC) thermoplastic-based material. The optical properties (UV/Vis and IR) of the capped luminescent CuCl films were studied as a function of time, up to 28 days and compared with bare uncapped films. The results clearly show the efficiency of the protective layers. Both COC and the PSSQ layer prevented CuCl film from oxidising while SiO_2 delayed the effect of oxidation. The dielectric constant of the three protective layers was evaluated at 1 MHz to be 2.3, 3.6 and 6.9 for C0C, SiO_2 and PSSQ, respectively.
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1. Introduction

CuCl belongs to the I–VII compound semiconductor material group with a zincblende structure at room temperature [1]. Its valence band is split into two bands by the spin–orbit interaction, yielding Z_{12} and Z_3 excitons. The excitonic binding energies are of the order of 190 meV and are much higher than those of III-Nitride or ZnO compound semiconductor materials [2]. It has a lattice mismatch of <0.4% when deposited on silicon substrates ($a_{CuCl} = 0.541$ nm and $a_{Si} = 0.543$ nm) [3] thus opening up the possibility of blue-UV optoelectronics on Si. In addition, the near lattice-matched silicon substrate suggests a possible advantage of CuCl/Si over the current blue-UV light-emitting materials. For instance the heteroepitaxy of GaN on $(0\,0\,0\,1)$ Al_2O_3 has a lattice mismatch as high as 13.9% [4], leading to the generation of misfit dislocations, which are deleterious to the performance of light-emitting devices produced thereupon.

CuCl has been previously used in the manufacture of electrooptic modulators and optical filters [5] and, as a candidate material for a blue-UV light-emitting devices, it will find applications across various industry fields. Typical

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possible applications include high-density optical storage, laser printing, projection displays, spectro-fluorometery, photo-catalytic reactions, counterfeit detection, chemical detection, traffic signals and in medicine (e.g. the use of UV radiation in treating cancer and cerebral apoplexy).

Recently, in our laboratory [6], we have grown and characterised wide band gap γ-CuCl material on Si substrates by physical vapour deposition for the purpose of fabricating a Si compatible light-emitting device. Despite their outstanding features and the potential applications of γ-CuCl thin films, their stability to moisture in ambient air is a major problem. Thin films of γ-CuCl oxidise completely into oxyhalides of Cu II within a few days of exposure to the ambient. In order to realise the practical use of this material an encapsulation layer is required.

Conventional encapsulation of γ-CuCl thin films by solid sealed glass at curing/deposition temperature greater than 250 °C cannot be used because CuCl chemically interacts with Si at a temperature greater than 250 °C [6]. Thus a low curing/deposition temperature, transparent and non-reactive protective layer is required to increase the longevity of this material. In this study we have investigated the behaviour of three candidate dielectrics for use as protective layers for thin films of γ-CuCl on Si substrates:

1. SiO$_2$ deposited by plasma enhanced chemical vapour deposition (PECVD). The PECVD grown SiO$_2$ has the advantage of low-deposition temperature, which favours low defect formation in the underlying substrate, low dopant diffusion and little degradation of metal layers [7]. The SiO$_2$ deposited using this method has found applications in film passivation, intermetal dielectric layers, in memory devices and in metal–insulator–semiconductor (MIS) devices.
2. Organic polysilsesquioxane (PSSQ) spin-on glass-based dielectric. PSSQ has been identified and recognised as a potential candidate for the next generation of low dielectric constant materials [8] in Si-integrated circuit technologies.
3. Cyclo olefin copolymer (COC)-based dielectric. COCs are thermoplastic polymers. Popular commercial producers of this material include Mitsui Chemical Company, Ticona (formerly Hoechst Celanese), Japan Synthetic Rubber and Zeon Chemicals Company. There are several types of commercial cyclo olefin copolymers based on different monomers and polymerisation methods. COCs are produced by chain copolymerisation of cyclic monomers such as 8,9,10-trinorborn-2-ene (norbornene) or 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (tetracylododecene) with ethene, or by the ring-opening metathesis polymerisation of various cyclic monomers followed by hydrogenation [9]. Owing to their rigid monomer units, COCs have low dielectric loss, low dielectric constant, low moisture absorption, good chemical resistance to polar solvents, low shrinkage, excellent transmittance in the visible and near-ultraviolet wavelengths and low birefringence [10].

Since the first report of the synthesis of COC in 1991 [11], it has found applications in optical, medical, electrical packaging and diagnostic containers.

The optical properties (ultra violet/visible and infra red) of the capped luminescent CuCl films were studied as a function of time for up to 28 days and compared with bare uncapped CuCl films in order to test the efficiency of the protective layers.

2. Experimental procedure

The CuCl thin film samples with typical thicknesses of ~300 nm were grown on Si (1 0 0) and quartz substrates using the vacuum deposition method at a base pressure of ~1×10^{-6} mbar. Prior to deposition the substrates were degreased in Decon$^®$ solution and organic solvents. The Si substrate was also deoxidised using hydrofluoric acid solution. Commercially supplied CuCl with 99.999% purity (Alfa Aesar) was evaporated from a quartz crucible at a deposition rate ~0.5 nm s^{-1}. Immediately after the evaporation of CuCl, the protective layers were then deposited on the films. PECVD SiO$_2$ layer was carried out using an oxygen/hexamethyldysiloxane (O$_2$/HMDSO) mixture in a parallel plate RF reactor at a frequency of 13.56 MHz. The O$_2$/HMDSO ratio was 10:1, while the RF power that determines the degree of excitation and fragmentation was kept constant at 350 W. The operating pressure was 10 Pa and the deposition time was 8 min. For the deposition of the organic PSSQ-based layer, the CuCl films were dipped in Emulsitone glass forming solution (Emulsitone Inc, USA). The resulting film was annealed under nitrogen ambient at 160 °C for a duration of 1 h. The cyclo olefin polymer (COC) layer was deposited by dipping CuCl films in COC solution (Brewer Science). The resulting film was annealed in nitrogen ambient at 175 °C for 15 min. The thickness of the protective layers was estimated to be 300 nm for the PSSQ layer and 400 nm for both the PECVD SiO$_2$ layer and the COC layer using a stylus profilometer. During all the experiments, the samples were stored in individual transparent containers and exposed to air. The spectra were taken after the fabrication of the samples and then after 7, 14, 21, and 28 days. For reference, the spectra of uncapped CuCl samples were studied along side the capped samples.

Absorption and IR measurements were carried out using a Perkin Elmer Lamda 40 UV/Vis spectrometer and a Perkin Elmer GX FTIR system. For electrical measurements, the protective layers were sandwiched between indium tin oxide (ITO) and aluminium electrodes, resulting in metal–insulator–metal (MIM) structures. The top electrode was Al with cross sectional area of 0.02986 cm^{-2} for both PSSQ and COC films and 0.09621 cm^{-2} for SiO$_2$ deposited by PECVD. Contacts were made to the electrodes by using an aluminium jumper wire of 0.025 mm diameter (Advent Research Materials Ltd) and quick drying silver paint (Agar Scientific). The

samples were mounted in a light-tight, earthed, steel vacuum chamber, allowing electrical characterisation at a base pressure of 10^{-5} Torr. AC electrical characterisation was performed with a Hewlett Packard 4284A 20 Hz–1 MHz precision LCR meter. Capacitance was measured as a function of frequency from 20 Hz to 1 MHz. All measurements (optical and electrical) were carried out at room temperature.

3. Results and discussion

3.1. UV/Vis spectra

The absorption spectrum for the uncapped film taken immediately after deposition is shown in Fig. 1(A), plot (a). This shows clearly the Z_{12} and the Z_3 excitonic absorption features, which are as a result of the valence band being split into two bands by the spin–orbit interactions [12]. The degradation of the film is detected by the enormous reduction and broadening of the excitonic peaks as can be seen in Fig. 1(A), plots (b) and (c). After 14 days the excitonic peaks disappeared, indicating a total oxidation of the CuCl film.

By examining the absorption spectra of Fig. 1(B)–(D), one can still notice the effect of oxidation on the CuCl

capped with PECVD SiO_2 while those encapsulated with PSSQ and COC are stable in the ambient. The PECVD SiO_2 layer reduced the kinetics of the CuCl deterioration process while organic PSSQ and COC layers prevented it.

3.2. IR spectra

Fig. 2 shows the IR spectra of the uncapped CuCl. The heteroepitaxially grown CuCl/Si structure was used for the background scanning, thus the as-deposited film gave a straight line spectrum. The major differences observed between the spectrum of the CuCl as-deposited and after 7 days of exposure to ambient are the intense double peaks centred around ~3336 and ~3444 cm^{-1}. This indicates the oxidation of CuCl to an oxyhalide of Cu II, which is as a result of CuCl reacting with moisture in ambient air [13]. This is likely due to the formation of weak bonds that exists in monovalent CuCl films. The oxidation increases as a function of time, which is consistent with the UV/Vis data. Similar to the uncapped film, oxidation does take place in films capped with SiO_2 deposited by PECVD as can be seen in Fig. 2(B). The only difference is that the oxidation rate has been reduced. Other major peaks in the SiO_2 spectra are related to Si–O–Si bonds occurring at 450 and 1070 cm^{-1} [14]. The inability of SiO_2 deposited by
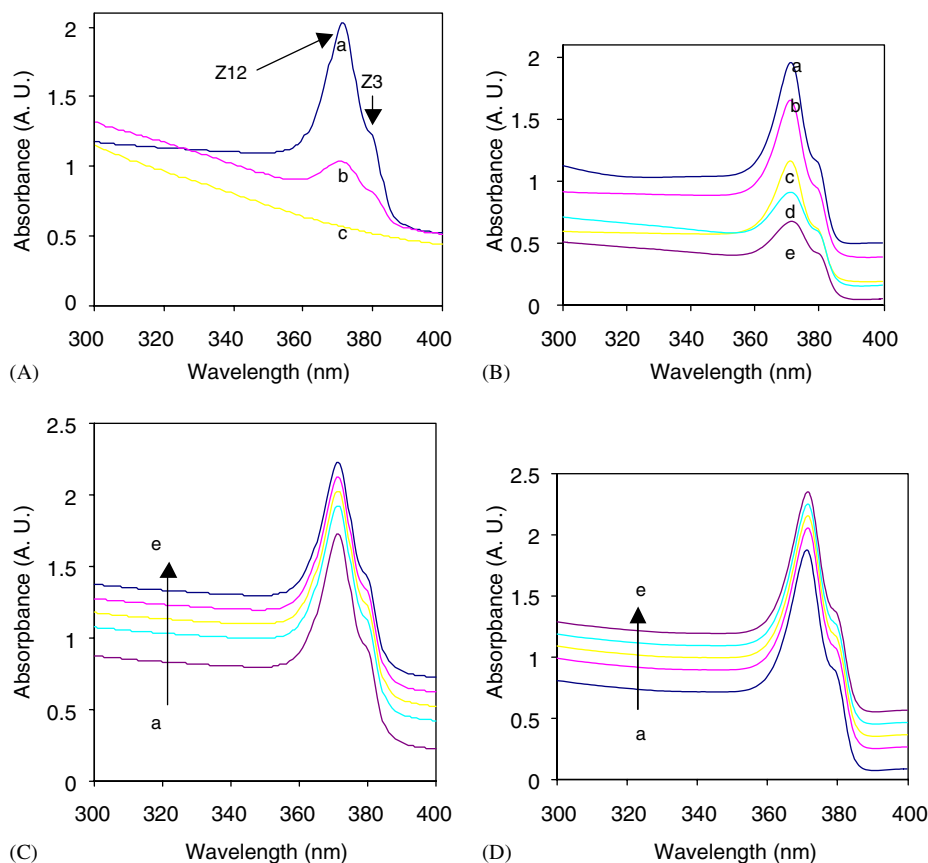

Fig. 1. Absorbance spectra: (A) unprotected CuCl film, (B) CuCl film protected with SiO_2, (C) CuCl protected with PSSQ, (D) CuCl protected with COC. The successive spectra were recorded after (a) immediately after deposition, (b) 7 days, (c) 14 days (d) 21 days (e) 28 days. The plots (a)–(c) are shifted with respect to each other in (C) and (D).
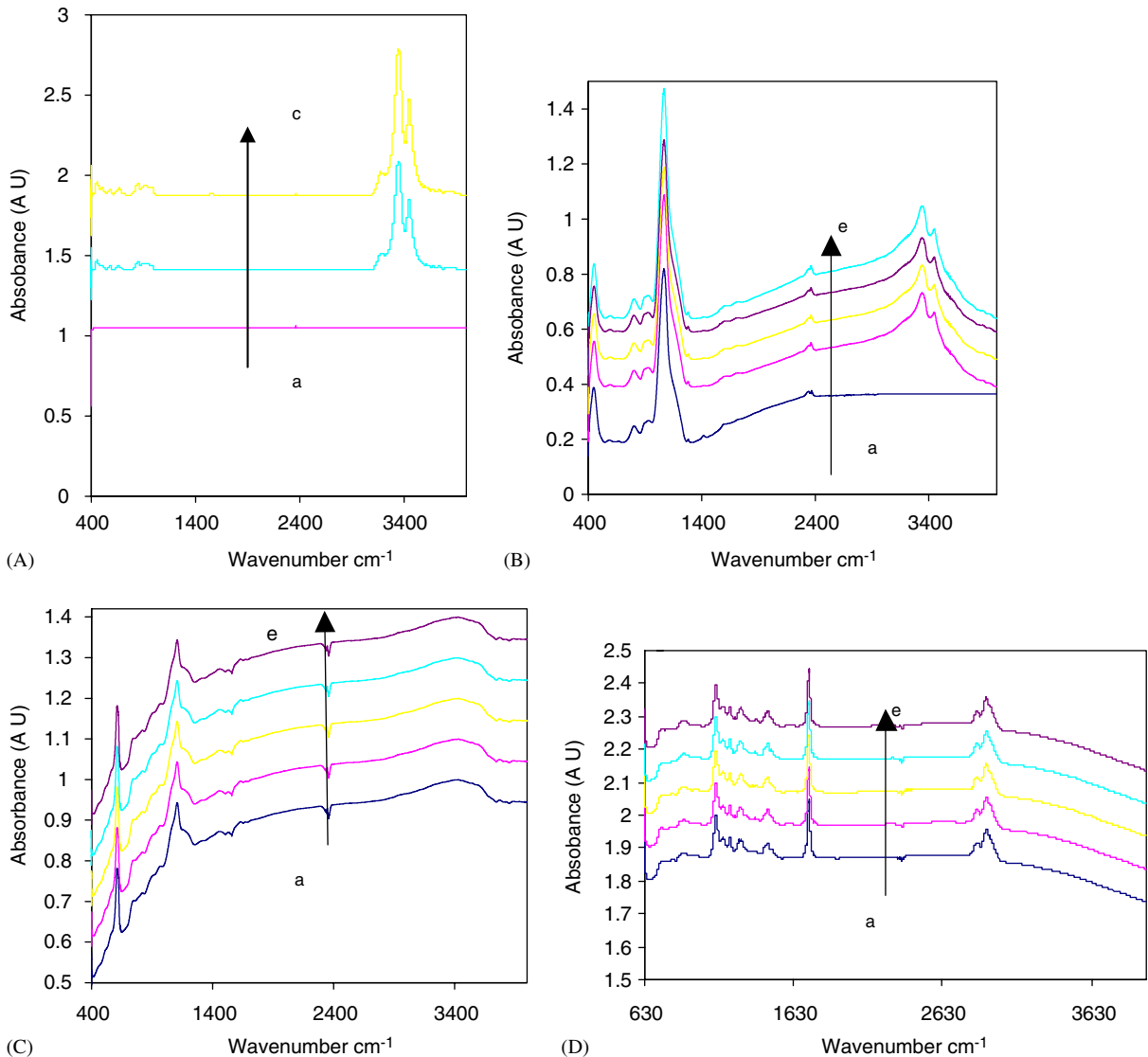
Fig. 2. IR spectra: (A) unprotected CuCl film, (B) CuCl film protected with SiO₂, (C) CuCl protected with PSSQ, (D) CuCl protected with COC. The successive spectra were recorded after (a) immediately after deposition, (b) 7 days, (c) 14 days, (d) 21 days and (e) 28 days, respectively. Plots (a)–(e) are shifted with respect to each other for clarity.

PECVD to encapsulate this material may be linked to excessive stress and adhesion problems between the SiO_2 and CuCl layers. This is usually observed by the formation of cracks on SiO_2-encapsulated CuCl films with a few hours of deposition.

Similar to the UV/Vis results, there is no evidence of oxidation in the films capped by PSSQ and COC, which is confirmed by the absence of the double peaks at ∼3336 and ∼3444 cm^{-1}. The major absorption peaks in the PSSQ capping film spectra include Si–C at 608 cm^{-1} [15], Si–O–Si occurring at ∼1090 cm^{-1} [7] and the broad band around 3200–3600 cm^{-1} is attributed to OH due to incomplete curing of the film. For COC, the several peaks occurring between 950–1225 cm^{-1} and the double peaks centered around 2917 and 2847 cm^{-1} are attributed to C–H absorption, the peak at 1459 cm^{-1} is the C=C–C

aromatic stretch while peak at 17290 cm^{-1} is the carbonyl C=O bond [16].

3.3. Dielectric constant

Fig. 3 shows the capacitance as a function of frequency for the three MIM structures, with a bias of 0.5 V (AC) superimposed on 10 V (DC). Analysing the capacitances of the protective layers, we have observed that the COC displayed an almost frequency independent capacitance. Similar to COC, the PECVD SiO_2 showed a fairly constant capacitance throughout the frequency range while the PSSQ layer showed a highly frequency-dependent capacitance at low frequencies. The electrical stability of the COC could be attributed to the rigid olefin units randomly or alternatively attached to the polymer backbone [10], while
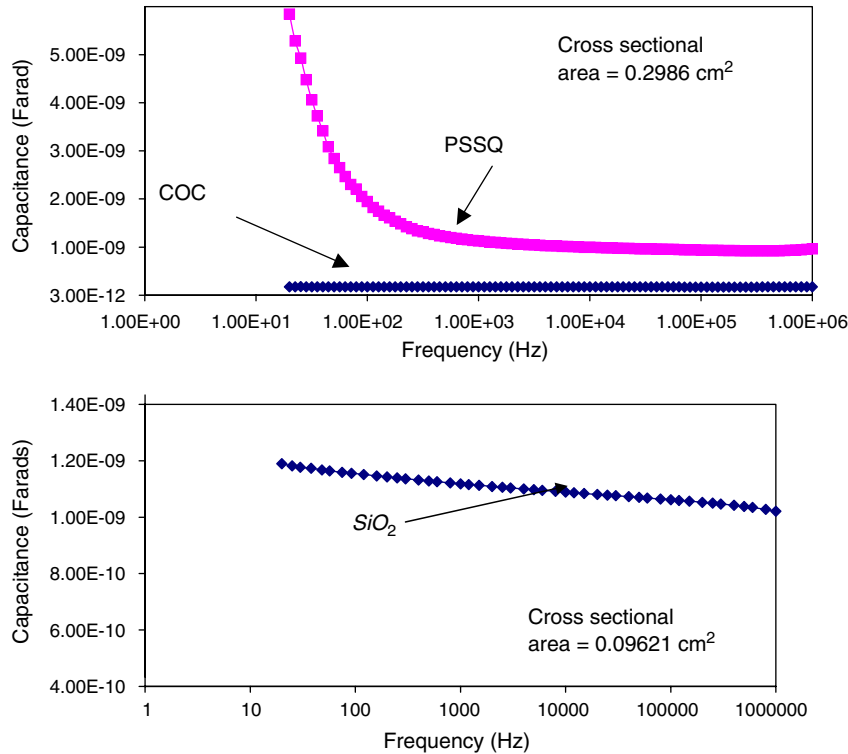
Fig. 3. Capacitance–Frequency plot for the protective layers.

the variation of the capacitance of the PSSQ may be linked to incomplete polymerisation and interfacial capacitance effect.

The relative permittivities (dielectric constants) of the protective layers were determined from the capacitance–frequency plot at 1 MHz to be 2.3, 3.6 and 6.9 for COC, PECVD SiO_2 and PSSQ, respectively. The high value of the dielectric constant of the PSSQ is most likely due to the presence of water (OH) in the insulator, whose dielectric constant is ~80 [17].

4. Conclusion

Thin film, luminescent, heteroepitaxial CuCl on Si oxidises into oxyhalides of Cu II on exposure to ambient air. This can be prevented by using protective layers that will insulate them against moisture and air. The UV/Vis and IR absorption measurements showed that both COC and polysilsesquioxane layers successfully encapsulated CuCl for lengthy periods of 28 days while PECVD SiO_2 slowed the rate but did not eliminate the oxidation. The high-frequency dielectric constants of the protective layers were estimated at 1 MHz to be 2.3, 3.6 and 6.9 for COC, SiO_2 and PSSQ, respectively. We are currently studying the ageing of CuCl films with different thicknesses of encapsulating layers, and for a period of up to 6 months. Early indications suggest that COC and PSSQ encapsulation will work for these extended time frames.

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