Copper Halide Semiconductors for Room Temperature Quantum Applications – A Materials Perspective

R.K. Vijayaraghavan, S. Daniels and P. McNally

School of Electronic Engineering, Dublin City University
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New Quantum Technologies

• Based on control and manipulation of quantum entities:
  – individual photons,
  – photons mixed with other physical particles, e.g. light-matter coupling,
  – excitonic, biexcitonic and polaritonic systems.
• Light-matter coupling can be implemented in the long wavelength red and infrared regions of the spectrum.
• “Spectral bottleneck” in the Blue/UV spectral region...350-450 nm.
• Precludes the fabrication of
  – useful Blue/UV ultra-low power (e.g. polaritonic) light emitting and laser diode sources,
  – the generation of room temperature quantum entanglement systems in the Blue/UV spectrum.
Quantum Quasiparticles

- **Exciton (Wannier):**
- Bound electron-hole pair
- Coulomb attraction

- Hydrogen-like bound states
- Binding energy $E_B \approx 10 \text{meV}$
- Bohr Radius ($a_B$) $\approx 100\text{Å}$

- Composite bosons

\[
E_b = -\frac{m^*_r q^4}{2\hbar^2 \varepsilon^2} \frac{1}{n^2}
\]

\[
\frac{1}{m^*_r} = \frac{1}{m^*_e} + \frac{1}{m^*_h}
\]
Quantum Quasiparticles

- **Biexcitons:**
  - Exciton molecules

Biexciton Binding Energies:
  - Typically \( E_{\text{biexciton}} = 1-5 \text{ meV} \) ...very small

- Also composite bosons.
Quantum Quasiparticles

• **Polaritons:**
• Light-Matter Coupling $\Rightarrow$ Microcavity
• Photons and Excitons couple
• Polariton-excitons $\Leftrightarrow$ “Polaritons”

\[ \gamma = \text{loss channel} \]
\[ \Omega = \text{coupling strength between optical transition of the material and the resonance photon mode} \]

Courtesy of P.G. Savvidis, Univ of Crete.
Bose-Einstein Statistics Prevail

The probability that a particle will have energy $E$

$$f(E) = \frac{1}{Ae^{E/kT} - 1}$$

Describing integer spin bosons, this distribution allows an unlimited number of particles to condense into a single level.

For photons, $A=1$, so the occupation of very low energy states can increase without limit.

The quantum difference which arises from the fact that the particles are indistinguishable.

The exponential dependence upon energy and temperature. See the classical Boltzmann distribution for more description.

Sources:
hyperphysics.phy-astr.gsu.edu
www.uni-muenster.de
imagebank.osa.org
Polariton Lasing

(a) Semiconductor microcavity: active layer, *e.g.* quantum wells (QWs) sandwiched between two distributed Bragg reflectors (DBRs).

(b) Exciton-polariton ("polariton") \( \rightarrow \) coherent superposition of an exciton and a photon.

(c) Polariton dispersion relation, showing the lower-polariton (LP) and upper-polariton (UP) branches.

- Visible radiation emission with frequency \( \hbar \omega_s \) is shown.
- \( k \)-axis is the wavevector axis of the exciton-polariton.
- The excited 2p exciton state with frequency \( \omega_p \) and terahertz transition with frequency \( \omega_c \) are also illustrated.

**Sources:** M. Glazov, SPIE Newsroom, DOI: 10.1117/2.1201212.004623 & H Deng et al., Rev. Mod. Phys. 82 (2010) 1489-1537.
Polariton Lasing

(a) Polaritons are excited by a pump laser.

(b) Strong coupling between the cavity photon and exciton dispersions split the dispersions near $k = 0 \Rightarrow$ creates a lower polariton (LP) and an upper polariton (UP) dispersions. Pump laser excites high energy excitons which cool via phonon emission towards the bottleneck region (black cloud). Excitons then scatter into the condensate via stimulated cooling.

Polaritonic Light Emitters

- Polaritons behave like electrons/holes with an effective mass \(\approx 1/10,000\) that of an electron!
- Different lasing mechanism possible \(\Rightarrow\) “polaritonic lasing”.
- Lasing threshold current densities 2-3 orders of magnitude lower than for conventional laser diodes (LDs).
  - **Conventional LD**: \(J_{th} = 10,000 \text{ Acm}^{-2}\)
  - **Polaritonic LD**: \(J_{th} = 100 \text{ Acm}^{-2}\)
- Ultra efficient; ultra low power light emission possible.
UV Entangled Photons

- **Resonant Hyper-Parametric Scattering (RHPS)**
- Generation of two entangled photons via electronically resonant third order nonlinear optical process.
- Copper halides - CuCl or CuBr - are ideal materials.
- RHPS resonant to biexcitonic state.
- Two pump photons (frequency $\omega_i$) resonantly create a biexciton.
- Biexcitonic state ($\Gamma_1$) has zero angular momentum, i.e. $J = 0$.
- Scattered ENTANGLED (daughter) photons ($\omega_s$, $\omega_{s'}$)
- Emerge from the $J = 0$ process.

UV Entangled Photons

- Actual RHPS emission process $\Rightarrow$ phase-matching condition involving polaritons.
- Biexciton coherently decays into two polaritons (sum of photon energies and momenta conserved).
- Lower energy polariton (LEP) and higher energy polariton (HEP).
- Polarisation entangled photons confirmed at 4 K by Edamatsu et al. (2004).

BUT...

- Optical pumping was used
- **ELECTRICAL PUMPING** preferred for field operation.
- P. Bhattacharya *et al.* (2014): Demonstrated room temperature electrically pumped GaN polaritonic LD.
- Current injection is orthogonal to the optical feedback direction of the resonator.
- $J_{th} = 169 \text{ Acm}^{-2}$. $\lambda \approx 365 \text{ nm}.$

Can we achieve superior operation?...

- Copper halide (CuHa) semiconductors possess much higher excitonic binding energies.
- The higher this energy the more likely is stable and continuous room temperature operation*.
- Biexcitonic binding energies are very high.
- More likely it is that the CuHa material can exhibit quantum entanglement effects, which are essential components of photonic quantum information processing and communication (QIPC) technologies.

** Excitonic structure comprises of a number of closely spaced excitons e.g. \( Z_{1,2} \) and \( Z_{3} \).

\&\& Typically achieved using quantum confinement e.g. multiple quantum wells (MQWs); CuHa data quoted is for bulk material but CuHa MQWs will see up to 5x enhancements [D. Ahn et al., Appl. Phys. Lett. 102, 121114 (2013)]


The Copper Halides

• $\gamma$-CuCl; $\gamma$-CuBr: I-VII, cubic, zincblende semiconductor.

• Direct, wide bandgap.

<table>
<thead>
<tr>
<th>Material</th>
<th>Room Temp. Bandgap (ev)</th>
<th>Exciton Binding Energy (meV)</th>
<th>Lattice Constant (nm)</th>
<th>Melting Point (Celsius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.12</td>
<td>-</td>
<td>0.538</td>
<td>1414°</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.37</td>
<td>60</td>
<td>0.324 (wurtzite)</td>
<td>1974°</td>
</tr>
<tr>
<td>GaN</td>
<td>5.43</td>
<td>23</td>
<td>0.438</td>
<td>2520°</td>
</tr>
<tr>
<td>CuCl</td>
<td>3.365</td>
<td>190</td>
<td>0.541</td>
<td>430°</td>
</tr>
<tr>
<td>CuBr</td>
<td>3.1</td>
<td>108</td>
<td>0.568</td>
<td>504°</td>
</tr>
</tbody>
</table>
Requirements for CuHa polaritonic/biexcitonic electrically pumped device operation

• High quality doped active CuHa nanolayers:
  – n-CuCl; p-CuCl
  – n-CuBr; p-CuBr.
• Electrical contacts to CuHa layers.
• Microcavity confinement for polaritons.
• Encapsulation to maintain device operation.

• Significant recent advances meeting each of these requirements.
n-type CuHa nanolayers: Zn doping

Zn Dopant: A group II element with almost similar ionic radii to Cu (≈ 60 pm)

Substitutional Zn in the Copper site

Cu vacancy

N- type CuCl

Zn is an excellent donor for CuCl or CuBr.
Deposition method

Pulsed dc magnetron sputtering of a CuCl:Zn target at room temperature.

- Working pressure \( \approx 5.5 \times 10^{-3} \text{ mbar} \)
- Power density \( \approx 1.75 \text{ W/cm}^2 \)
- Pulse duty cycle \( \approx 40\% \)

Advantages

- High deposition rate
- Manufacturability
- Good quality films

XRD spectra of CuCl: Zn films

XRD of CuCl:Zn films developed from (a) 0, (b) 1, (c) 5 and (d) 3 wt % Zn doped targets and the intensity variation of (111) orientations (Inset)
Low temperature PL spectrum

PL spectrum at 80 K and at room temperature (inset) of a typical sample developed from 3wt % Zn doped target
Electrical properties

For 3% (w/w/) Zn

- Carrier concentration $\approx 9.8 \times 10^{18} \text{ cm}^{-3}$
- Carrier mobility $\approx 0.1 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$
- Resistivity $\approx 6 \Omega \text{cm}$
p-type CuHa nanolayers: O doping

- Deposition pressure $\approx 3 \times 10^{-5}$ mbar
- Power $\approx 300$ W
- Plasma chamber pressure $\approx 6.6 \times 10^{-2}$ mbar

Physical Vapour Deposition (PVD) of CuBr powder followed by oxygen plasma treatment of the film

p-type CuBr: Structure and Transparency

XRD pattern of the CuBr:O films

Photograph of the p-type CuBr film
Electrical & Optical Properties

Hole concentration and mobility

1 min plasma exposure

- Carrier concentration $\approx 8 \times 10^{18} \text{ cm}^{-3}$
- Carrier mobility $\approx 0.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$
- Resistivity $\approx 1.5 \Omega\text{cm}$

PL spectra of the ASD and oxygen doped CuBr film
Electrical contacts to CuHa layers

- **Reversible Cu contacts**: Cu$^+$ ions can be rapidly replaced with Cu.
- **Irreversible Au**: Cannot replenish Cu$^+$ ions → blocking electrode, non-Ohmic behaviour.

Microcavity confinement for polaritons

- Distributed Bragg Reflectors (DBRs) are used:
- HfO$_2$/SiO$_2$ alternating layers (each layer tens of nm thick)
- Growth is typically on Al$_2$O$_3$ (0001) substrate.
- The effective active layer length is tied to the resonant wavelength of the CuHa excitons in vacuo and the background dielectric constant.
- Typical CuHa layer thicknesses of the order of 100 nm.
- DBRs and the CuHa: Physical vapour deposition.
- Angular dependence of reflectance spectra on incident light is used to prove the cavity polariton dispersion.
- Angle-resolved PL spectra are also used to confirm same.

CuBr Microcavity Polaritons

- CuBr active layer (thickness = \(\lambda/2\)) was sandwiched by the DBRs.
- \(\lambda = \lambda_{\text{EX}}/\sqrt{\varepsilon_b}\) in a bulk microcavity; \(\lambda_{\text{EX}}\) is the resonant wavelength of the lowest lying exciton in vacuum, and \(\varepsilon_b\) is the background dielectric constant.
- \(\lambda/2 = 88\) nm, and \(\varepsilon_b = 5.7\).
- DBRs = HfO\(_2\)/SiO\(_2\) (9.5 periods (top) and 8.5 periods (bottom))
- Four cavity-polariton modes: Lower Polariton Branch (LPB), Middle Polariton Branch 1 (MPB1), Middle Polariton Branch 2 (MPB2), and Upper Polariton Branch (UPB) in order of energy
- Incidence-angle PL dependence of the energies of the four cavity-polariton modes.
- Solid curves depict the fitted results with theory.
- Dashed horizontal lines indicate the exciton energies, and the dashed curve shows the cavity-photon dispersion.

Advantages of CuHa for Polariton Lasing

Number of active region Quantum Wells (QWs)

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>CdTe</th>
<th>CuCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bohr Radius in QW (Å)</td>
<td>90</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>Binding Energy (meV)</td>
<td>10</td>
<td>25</td>
<td>190</td>
</tr>
<tr>
<td>Saturation Density of Lower Polaritons (10¹⁰ cm⁻²)</td>
<td>4</td>
<td>50</td>
<td>20,000</td>
</tr>
</tbody>
</table>

Use of multiple QWs – enhances E-field/exciton overlap

$$\Omega_{\text{Rabi}} \propto \sqrt{N_{\text{QW}}}$$

$$n_{\text{exc}} \propto 1/N_{\text{QW}}$$ for a given polariton population

Use of excitons with small Bohr radius

$$n_{\text{sat}} \propto 1/a_B^2$$

Adopted from:

Use of excitons with small Bohr radius

1 QW (pn junction) for CuHa?
Multiple Deposition Possibilities

• Thin (<100 nm) CuHa nanolayers can be deposited using:
  – Physical Vapour Deposition (RF / Pulsed DC magnetron sputtering)
  – Electron beam deposition
  – Atomic layer deposition

• All produce CuHa materials of sufficient quality to confirm polaritonic modes and the presence of biexcitons.

Device Encapsulation

- Polysilsesquioxane-based spin on glass material (PSSQ).
- Cyclo olefin copolymer (COC) thermoplastic-based materials.
- CuCl optical properties unaltered for up to 28 days.

Absorbance spectra: (a) immediately after deposition, (b) 7 days, (c) 14 days, (d) 21 days, (e) 28 days. [Plots shifted with respect to each other for ease of visibility.]

Other Growth Options

• Hybrid organic-inorganic spin-on-glass CuCl films
  – PSSQ/CuCl.

Vapour Liquid Solid (VLS) Growth of CuBr/KBr Microdots

KBr ‘Spots’

Evaporated CuBr

~350nm CuBr evaporated film on Si

 Shadow Mask

Source: A. Cowley et al., EMRS Spring, 2011.
Intermixed CuBr/KBr Microdot VLS Formation

- After shadow mask deposition of KBr, films are annealed at 220° C under vacuum.
- In addition, a small flux of CuBr is provided.
- The CuBr/KBr phase diagram shows that a eutectic solution will form at approximately 170°C.
CuBr/KBr Intermixed Microdot

- Inspiration: Silicon ‘whiskers’ grown using VLS type growth since the early 1960’s.
- Nanowires /nanorods ⟷ single crystals with fewer imperfections.
CuBr/KBr Microdot Array
Room Temperature PL Enhancement

- Observed luminescence improvement is based on the migration of Cu+ and K+ ions within the film.
- Crystalline imperfections can act as recombination centres, trapping electrons and holes and reducing the effective carrier concentration for emission processes.
- Displacement of the Cu+ and K+ ions, driven by their chemical affinities for negative ions (i.e., the Br⁻ anion), can close some of the vacancies present [1].
- Can result in a net improvement of the emission intensity, as observed.

325nm He-Cd laser, 0.3 sec acquisition

Room Temperature PL Enhancement

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**Source:** A. Cowley et al., EMRS Spring, 2011.
Where next?

- Excellent progress in CuHa materials processing in past decade.
- Opportunity to develop new science, technology and devices.
- Quantum manipulation of light and matter for blue/UV (350-450 nm).
- Electrically pumped microcavity structures.
- Ultralow power blue/UV light emitters.
  - Exciton, biexciton and polariton control.
  - Potential for quantum entanglement.

**Applications:**
- Medical and biodiagnostics: new capability in point of care diagnostics;
- Computing: extremely low power optical interconnects;
- Telecommunications: THz speed optical spin switching;
- Security/cryptography: quantum entanglement for quantum information processing communications;
- Who knows???
THANK YOU!!!
Exciton Polariton Dispersion, Normal Mode Splitting and Oscillation
[H. Deng et al., BaCa Tec-Summer School, Würzburg, Germany (2005)]

Polariton dispersion curves


GaAs/AlGaAs Systems

CuBr/Si heterojunction for photovoltaic applications

I-V characteristics in dark and under illumination

Efficiency of \( \approx 2.1 \% \) with AM1.5 illumination

Figure 1 | Schematic sketch of the polariton microcavity LED. a, The structure consists of a 5L/2 cavity surrounded by two doped GaAs/AlAs DBRs. Dry etching was used to expose the p-DBR, forming round mesas of 400 μm diameter. To enable light emission from the front side, a ring-shaped p-type ohmic contact was deposited on the top of the mesa, and the n-type contact was deposited on the back side of the substrate. QW, quantum well. Current source A is used to bias the device. b, Electric field and refractive index distribution along the structure. Elevated temperatures necessitate the use of three pairs of In0.5Ga0.5As/GaAs quantum wells placed at the antinodes of the electric field to enhance the exciton oscillator strength required for strong coupling.


Polariton Device Structures

Figure 1 | Quantum well microcavity polariton diode and characteristics.
a. Schematics of an electrically contacted 20-μm-diameter micropillar with four quantum wells (QWs) in the cavity, sandwiched by gradually doped distributed Bragg reflectors (DBRs). b. Waterfall plot of reflectivity spectra showing anticrossing on the detuning map. a.u., arbitrary units; LP, lower polariton; UP, upper polariton; C, photonic cavity mode. c. Microphotoluminescence spectrum of the fundamental mode of a highly photonic micropillar cavity with a diameter of 2 μm and $Q = 6,320$. 