Three strategies for fabrication of I-VII semiconductor nanostructures

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Three methods of I-VII nanoparticle/nanostructure synthesis/fabrication as applied to AgI and AgI-CuI solid solutions (1) hot solution controlled precipitation, (2) mechanoochemical reaction for metastable nanopowders such as γ-Agl and (3) controlled iodization of Ag, Ag-Cu and Cu nanostructured thin films using a specially fabricated hourglass iodinator jig, are briefly outlined. They have applications in sensor and optoelectronic technologies. Focused though on I-VII semiconductors, they are equally applicable to chalcogenides and chalcohalides of transition and post-transition metals. These materials are used to investigate such exotic physics as stress-induced confinement of excitons in thin films and plasmon-exciton ‘transitions’. The efficacy of brief iodization for a modification of nanostructured Ag surfaces for photonic applications has recently been demonstrated. III-V and II-VI-type nanostructures could as well be fabricated and studied for I-VII semiconductors and their chalcogenide combinations I-VII-VI-an area that beckons the explorer and the exploiter.

Keywords: Nanoparticles, Semiconductor, Fabrication, Sensor, Optoelectronics

1 Introduction
Nanoscale synthesis of materials—in fluid media or unconsolidated dry powder or as low-dimensional thin film structures on substrates or in tubes (such as carbon nanotubes) are all endeavors in metastable materials science based on one single problem of third order (or higher) complexity namely precipitation and crystallization-involving shape, size and grain density as parameters to be ascertained and controlled. Thus, it is a contemporary challenge whose success can allow the nano-industry to move on. By way of conceptualization and a working mandate, it is vital to briefly consider tetrahedrality—a unique concept in nanoscience and nanotechnology. The tetrahedron is one of the perfect geometric shapes naturally occurring in the macroscopic world of matter. Tetrahedrality of the chemical bond arising from the microscopic reality of the carbon and carbon-like atoms is at once a dynamic attribute symbolizing material evolution itself-nanomaterial evolution through a specific 3D growth process in the current context. Tetrahedrality assures 3D connectivity in general but flexible tetrahedrality promises much more in the fascinating world of dimensions lower than three. Bond tetrahedrality and hybridization put together enable us to understand, explore and predict many things in the realm of non-equilibrium world of nanomaterials, such as phase stability, phase transitions and nanocrystallization. Quantum reality and thermodynamic necessity together make tetrahedrality a geometrical design template cutting across the organic and inorganic worlds of rational (nano)materials design and development. A dramatic manifestation of the flexible tetrahedral bond visualized as a ‘glassy-chemical bond’ occurs in the sol-gel synthesis of a silicate glass based on tetra-ethyl orthosilicate as discussed earlier1. The Ag/Cu-I bond is an unusual tetrahedral 70% ionic 30% covalent bond and the covalency arising from metal d-halogen p-hybridization that makes the I-VII’s AgI and CuCl, CuBr and CuI superionic conductors as well as large gap (~2.8 eV) semiconductors—a kind of Janus-faced compounds.

It is not easy to obtain an array of say uniformly-sized metal nanoparticles such as silver on a ‘workhorse’ kind of substrate such as Si as demonstrated by a recent study2. Even trivial precipitation reaction in water medium such as given in Eqs (1) and (2):

\[
\text{AgNO}_3 + \text{KI} \rightarrow \text{AgI(ppt)} + \text{KNO}_3 \\
2\text{CuSO}_4 + 4 \text{KI} \rightarrow 2\text{K}_2\text{SO}_4 + 2 \text{CuI} + \text{I}_2
\]

does not yield monodisperse AgI nanoparticles unless nontrivial strategies such as specific precursors/media3 and “boiling solution of KI added dropwise” are employed4. Chemical doping,
mechanoochemical synthesis, and novel techniques such as oxidative surface modification could be employed to create applicable nanoparticles and structures.

AgI_4 and CuI_4 tetrahedra (and also their chalcogen counterparts) (Fig. 1) with marginal (~30%) covalency are perhaps the only two unique building blocks that remind you of benzene in organic chemistry. Deep physics—not fully explored and much nanotechnology not yet fully exploited could be based on these inorganic counterparts of benzene! Water insolubility, mechanical softness and the nascent nature of the oxidizable (iodization and sulphidation to be specific) noble metal surface are the key characteristics that enable nano-scale synthesis. This paper focuses on three case studies. We note in passing that although we are dealing with I-VII semiconductors in present paper. These or allied concepts are at work in the synthesis of say CdS or CuSbS_2 which are of course involved in solar energy conversion or CuS which is the potential new thermoelectric material.

2 Precipitation Synthesis of I-VII Nanoparticles and Solid Solutions

The basis of this synthesis is the extreme water insolubility of silver iodide: the saturated solution at 298 K is 2.4 × 10^{-7} normal or 0.056 mg/L). Its solubility in ammonia is much less than that of the chloride or the bromide; the tendency to complex formation is not strong enough to overcome the effect of the extremely small solubility product. However, silver iodide is moderately soluble in sodium thiosulphate and in concentrated hydrochloric acid. Copper iodide does marginally better: 22×10^{-7} normal\(^5\) or 0.42 mg/L.

Solid solutions of AgI and CuI with zincblende or sphalerite structure may be prepared so as to change the property of the material in a single component. This is possible because of the extended mutual solid solubility range of AgI and CuI despite their unequal ionic radii ($r$Ag=1.26 Å; $r$Cu=0.96 Å; $r_{Ag}/r_{Cu}=1.31$). This large size mismatch in mobile cation size points to the possibility of a mixed mobile ion (Ag\(^+\) and Cu\(^+\)) effect controlled ionic conductivity in the AgI-CuI system. Furthermore, the fact that CuI is an electronic conductor in the temperature range of investigation brings into play factors such as $p$-$d$ hybridization to the conduction process—essentially including subtle changes in ion mobility and concentration. Non-trivial modification of the cation sublattice in the zincblende/bcc phases and the possibility of realizing interfacial polytypes are expected to decrease the defect concentration ‘$n$’ and hence the conductivity ‘$\sigma$’ of the high temperature $a$-phase thereby increasing the ‘$T_s$’ of AgI. Thus, the nanoparticle synthesis is connected with fundamental issues such as metal-halogen bonding, defects, polymorphism and applicable physical properties such as ionic conductivity.

The solubility difference between CuI and AgI has been utilized in the synthesis of solid solutions using the simple conversion process in an aqueous suspension to synthesize Ag\(_{1-x}\)Cu\(_x\)I ($x=0.05, 0.10, 0.15, 0.2$ and $0.25$) compositions. These samples were prepared by the gradual addition of the required molar aqueous solutions of the nitrates of silver and copper (Analar grade, LOBA, India) under continuous stirring and precipitating them with a 2 to 5% excess solution of potassium iodide (LOBA, India) just below the normal boiling temperature. After several decantations with double distilled water to remove the excess nitrates present if any, the samples were dehydrated in an oven at 60 °C for several hours. Fig. 2 shows typical X-ray powder diffractograms (Cu-K\(_\alpha\) radiation) evidencing formation of a zincblende phase of the Ag-rich Ag\(_{1-x}\)Cu\(_x\)I solid solutions ($x=0.05, 0.10, 0.15, 0.20$ and 0.25).

Dilatometry and high-temperature X-ray diffraction experiments on these samples have enabled a successful search for a zero-thermal expansion material in this system\(^6\) and a detailed phase diagram study\(^7\), respectively.

Liu et al\(^{8}\) have recently described a simple and efficient method for preparing homogeneous nano-Ag\(_{1-x}\)Cu\(_x\)I ($x=0-0.5$) solid solutions with wurtzite structure. The single-phase formation is attributed to

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Fig. 1 — Solid-state structure and the tetrahedral bonding with 3D connectivity that relate metal-halide and metal-chalcogenide materials such as AgI, CuI, Ag\(_2\)S and Cu\(_2\)S. The size and charge of the respective ions, the d-electron count of the cations, and the type of $A$–$X$, $A$–$A$, and $X$–$X$ bonding interactions are involved in nanosynthesis [after J D Martin et al., Chem Mater, 10 (1998) 2699.]
the active role of citric acid participating in the chemical reactions leading to the controlled synthesis of these compositions. It is interesting and worthwhile to examine systematically the specific role of citric acid which also happens to be an important fuel in combustion synthesis of nanomaterials.

Silver nitrate (AgNO$_3$) and copper nitrate (Cu(NO$_3$)$_2$) and potassium iodide (KI) and citric acid (C$_6$H$_8$O$_7$) of analytical reagent grade were dissolved in deionized water by agitation, respectively. Corresponding to series of the final nominal composition of the Ag$_{1-x}$Cu$_x$I solid solutions ($x=0.05, 0.10, 0.15, 0.20$ and $0.25$) aqueous solutions with different contents of AgNO$_3$ and Cu(NO$_3$)$_2$ were mixed together to obtain precursor solutions with the total metal concentration of 0.1 M. C$_6$H$_8$O$_7$ as the chelating agent was added to the precursor solutions according to cation concentration. Under the condition of continuous stirring and its normal boiling temperature, 2–5% excess aqueous solutions of KI with the concentration of 0.1 M were added drop wise to the solutions with different contents of AgNO$_3$ and Cu(NO$_3$)$_2$ and C$_6$H$_8$O$_7$. The desired solid solutions powders were obtained. Then, the powders in the aqueous solution were filtered and washed repeatedly with de-ionized water to remove the byproducts of the chemical reactions such as potassium nitrate and citric acid. Wet powders were obtained which were dehydrated in oven at 80°C to obtain powders ready to use for measurement or application.

3 Mechnanochemical Synthesis

Mechanochemistry — An essentially ‘dry’ processing route-exploits the effects of non-hydrostatic mechanical stress and plastic strain on the chemical processes inducing (a) change of the energy and entropy (b) change of the structure and chemical composition of molecules, crystals and other aggregates of matter.

Mechanochemical effects directly stem from the directional character of mechanical stresses. Purely mechanical forces could selectively break and re-form covalent bonds in individual molecules, thus promoting or depressing the chemical reactivity of covalent systems. Although in many of the solids, mechanical forces cannot be selectively applied to individual chemical species located at the sites of the crystalline lattice, localized mechanical stresses can still affect a relatively large volume due to the interaction forces operating across the lattice. Therefore, atomic, ionic, or molecular solids could all exhibit a cooperative response to mechanical deformation. Mechnanochemical effects directly stem from the interaction operating across the lattice. Therefore, atomic, ionic, or molecular solids could all exhibit a cooperative response to mechanical deformation. For example, the absence of direct chemical bonds between individual molecules, as well as the weakness of intermolecular forces, permit the plastic deformation of molecular crystals at low mechanical stresses. Molecules can be displaced from their original position and the crystalline lattice has been considerably disordered, without any noticeable chemical behaviour due to the activation of intramolecular bonds. Conversely, the chemical behaviour of metallic phases is intimately connected with their plastic deformation. In the regions of solid in which mechanical stresses are more intense, unusual mass transport processes take place, which induce in turn the intimate mixing of atomic species. Coordination shells are severely affected, finally resulting in new crystalline or polymorphic or amorphous chemical systems.

Ionic crystals can exhibit in principle a broader spectrum of behaviour. Cations and anions strongly interact with each other through very intense
electrostatic forces, resulting in high cohesive energies. At the same time, the intensity of electrostatic forces also results in the brittle character of ionic crystals. Even relatively small deformations can produce a brittle fracture as a consequence of the intense repulsive forces arising when ions of the same charge face with each other. On this basis, it can be expected that ionic crystals could be significantly reduced in size during the mechanical processing, which has been experimentally observed—this is the basis for mechanochemical reactive synthesis of nano superionic conductors.  

Although aforementioned behaviour is common to all of the ionic crystals, more variable responses to deformation can be obtained when either cations, or anions, or both, exhibit relatively complicated structures, strongly suggesting the extension of the mechanochemical reactive synthesis to transition metal and post-transition metal chalcogenides [for Cu$_{2-x}$S see Ref. (12)] and chalco-halides. The intense electrostatic forces arising from deformation processes can significantly destabilize the molecular ions. Deformation can give rise to intense intramolecular stresses originating from electrostatic repulsion and attraction which can potentially activate the rupture of covalent chemical bonds and then induce a strongly localized chemical reaction. This mechanism could also produce metastable paramagnetic centers such as Ag-based hole and electron centres probed by EPR in mechanochemically synthesized zincblende AgI nanoparticles.  

A remarkable example of mechanochemical synthesis is the realization at ambient temperature of the complete set of solid solutions in the system AgI-CuI. Not only does this method yield a ready-to use applicable nanopowder to applications such as electrochemical sensors and solid electrolytes, it has provided an opportunity to investigate phase diagram, phase stability and phase transitions. Significantly, it has illustrated how Cu as acted as an agent to reduce the particle size of the solid solutions [Fig. 3(a)].  

Compositions corresponding to AgI, Ag-rich (Ag$_{1-x}$Cu$_x$I where $x = 0.05$; i.e. 5%, 0.10, 0.15, 0.25), intermediate Ag$_{1-x}$Cu$_x$I ($x = 0.50$); Cu-rich (Cu$_{1-y}$Ag$_y$I, $y = 0.05$: 0.10, 0.15, 0.25) portion of the AgI–CuI system and CuI were synthesized by mechanical grinding in a 6-inch diameter agate mortar and pestle for 5 h at room temperature in an unilluminated room by using appropriate quantities (in wt%) of copper (LOBA, India), silver (Special materials project, Hyderabad, India) and I (Rasayana Laboratory, India). When attrition was carried out, the charge (Ag or Cu or I or Ag + Cu or Cu + Ag or Ag + Cu + I or Cu + Ag + I) present at the bottom of the mortar is sheared.
by the pestle at the start of the spiral type motion executed by it. This motion causes the charges to spread over the inner surface of the mortar, say 1/3 of the inner surface area (294.5 cm$^3$). In about a minute of attrition, the charge undergoes ‘reactive mixing’ as the pestle circles about 60 times in the mortar—a motion that is fairly uniform and periodic. The periodic motion of the pestle causes Ag/Cu grains to get compressed and the compressed surface is exposed to iodine molecules on the breaking-up and sublimating iodine flakes. This is but a simple-minded description of a process that deserves not only a detailed fundamental investigation but also a computer simulation such as molecular dynamics. Note that the exceptional stability of the iodine molecule and the easy vibrational excitability and the fact that room temperature is already higher than the triple point if iodine all combine to produce nanoparticles of these relatively soft solids AgI and CuI and their solid solutions possessing zincblende structure.

4 Partial/Complete Iodization of Ag and Ag-Cu Nanostructured Films

Silver nanostructured films fabricated by thermal evaporation or RF sputtering among a host of other techniques are perhaps the most investigated structures among metal nanostructures. It was realized during our earliest investigations$^{14}$ that these Ag (and later Ag-Cu and Ag-Sb ‘alloy’ films$^{15,16}$ offer a very versatile and fascinating platform to fabricate at ambient temperature and pressure I-VII nanostructures that could serve to investigate electronic structure development as well as to develop optoelectronic/photonic devices. While partial iodization creates metal-semiconductor nanocomposites complete iodization creates applicable nano semiconductors. This technique could be extended to the fabrication of nanoparticle arrays, nanowires, I-VII versions of quantum wells, ternary superionic conductors based on Ag and Cu as well as to investigate novel superionic superlattices—an area waiting to be explored.

How is this iodization implemented? The Ag or Ag-based alloy/multilayer film is fabricated in the usual way either by vacuum thermal evaporation onto suitable substrates (glass, quartz, PVA among others) and characterized by diffraction and microscopy. Subsequently they are mounted on top of a closed (airtight but with provision of gas passage/evacuation if required) hourglass iodinator (Fig. 4). Suitably weighed Iodine charge (flaky crystals) is placed at the bottom of the jig. The process begins right away and can easily be timed. Interruptions help ex-situ monitoring of partially iodized Ag films by XRD and microscopy. How does the process occur? We have looked at the kinetics of iodization and modeled it$^{17}$ as an interface-controlled reaction somewhat like the oxidation of silicon. Plasmon-exciton ‘transitions’ in RF sputtered ultrathin films (<20 nm average
thickness) which involves the initial formation of surface plasmons (note that the films are rough/disordered) and their gradual conversion to the so-called Z_{1,2} and Z_3 excitons^{8,10} of zincblende AgI have been investigated. In a recent work^{20}, plasmon-exciton transitions in iodized RF sputtered Cu thin films have been investigated (see Fig. 5 for AFM picture).

Our recent studies on Ag films^{21} have shown that short-term (< 10 min) iodination^{22} can be an easy but effective method for creating Ag nanoparticle assemblies of controllable median particle size for applications such as fabrication of SERS-active substrates. This method is perhaps superior in that it does not involve messy solutions and there is no need to generate^{22} wurtzite AgI.

5 Conclusions
In this brief overview, we have outlined three methods of nanoparticle/nanostructure synthesis/fabrication as applied to AgI and AgI-CuI solid solutions: (1) hot solution controlled precipitation, (2) mechanochemical reaction for metastable nanoparticle synthesis (zincblende AgI and AgI-CuI solid solutions) and (3) controlled iodization of Ag and Ag-Cu and Cu nanostructured thin films. Theses I-VII semiconductors/superionics have applications to sensor and optoelectronic technologies. Though we have focused on I-VII semiconductors, they are equally applicable to chalcogenides and chalcohalides of transition and post-transition metals. Although not discussed here, we have used these materials to investigate such exotic physics as stress-induced confinement of excitons in thin films and plasmon-exciton ‘transitions’. We have recently demonstrated the efficacy of brief iodization for a modification of nanostructured Ag surfaces for photonic applications. III-V and II-VI-type nanostructures could as well be fabricated and studied for I-VII semiconductors and their chalcogenide combinations I-VII-VI-an area that beckons the explorer and the exploiter.

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References


