Abstract

While bridging the gap between the atomic structures and bulk matters, nanomaterials are of great interests for fundamental understanding as well as for different application perspectives. In this article, it is proposed to provide a review regarding various synthesis processes of nanomaterials, growth mechanisms and a range of experimental techniques to discuss remarkable properties of materials at the nanoscale dimensions. Equilibrium (ambient or vacuum thermal annealing) as well as non-equilibrium (for example, utilizing ion-beams) methods are elaborated for the processing of nanomaterials. Here, nanomaterials stand for species of metal nanoparticles, bimetallic alloy nanoparticles or composite materials of metal nanoparticles in different oxide semiconductors. Akin to the pure metal nanoparticles, alloy metal nanoparticles exhibit exciting optical responses. For example, surface-plasmon resonance frequencies of bimetallic alloy nanoparticles are tunable in controlled fashions through the variation of alloy compositions. Metal nanoparticles in semiconductors are discussed to elucidate examples of quasi-particle interactions between plasmons and excitons in the composite as well as interesting photoluminescence properties of the nanomaterials. Thermal stability of semiconductors and growth of the nanoscale metal particles in the composites are found to play crucial roles in this regard. Depending on the growth of metal nanoparticles, for instance, photoluminescence intensity of semiconductors is observed to be enhanced or quenched in the metal-semiconductor composite nanostructures.

Keywords

Nanomaterials, Ion beam, Thermal annealing, Optical, Photoluminescence, XPS, XRD

Introduction

At nanoscale dimensions, metals, bimetallic alloys and semiconductors (quantum dots) exhibit remarkable materials properties which are completely unknown in their bulk counterparts. As an outcome, great lots of research interests are shown from different perspectives: materials synthesis, fundamental understanding as well as from application point of view. Nanomaterials, as we know, are no way different compared to the parent phase of materials except
its’ physical dimensions. Dimensions of nanomaterials range between 1-100 nm, at least in one direction. According to the definition, at nanoscale dimensions physical, chemical and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matters. Many interesting physical properties (for example: optical, vibrational, structural, transport, photoluminescence etc.) unfold at nanoscale dimensions of matters. These phenomena occur in nanomaterials because of different reasons like, i) quantum-confinement effects, ii) larger surface area compared to bulk materials of comparable masses, iii) restrictions due to translational invariance in nanoscale crystal lattices. Take, for example, eye-catching colors of decorative arts in church glasses or Lycurgus cups. The first insight regarding such beautiful colors of stained-glasses was published by Michael Faraday in 1857 [1]. Appearance of the striking colors was theoretically explained later (after 50 years) as a result of resonant absorption of light in finely dispersed metal particles [2]. One of the intriguing observations is that nanoscale metal particles display strong optical absorptions in the UV-visible wavelength range of light. The emanating deep hues from such samples bear a close resemblance of materials like, for example, molecular dyes [3, 4].

The resonant absorption of light which arises due to collective oscillations of the conduction electrons in metal particles is being described as the localized surface-plasmon resonance (SPR) in scientific literatures [5, 6]. SPR frequency is characteristic of the metal through its intrinsic dielectric function. Apart from it, SPR responses depend strongly on sizes, shapes of plasmonic nanoparticles and dielectric constants of the media [7]. Quanta of collective oscillations of conduction electrons in metals are plasmons [8]. The word SPR signifies that the conduction electrons are primarily localized over the surface of metal nanoparticles under the influence of electric field of light (Figure 1). Under the assumption of quasi-static size regimes (i.e., particle sizes << wavelength of light), nanoparticles may experience a homogeneous field across the particle. The field induces collective oscillations of free electrons in metal or alloy metal nanoparticles against the background of positive charge of nucleus in metal atoms. As a result, oscillations of electric dipoles are induced. The resonant dipolar optical absorption takes place when oscillations of the electric dipoles match with the excitation frequency of light. Optical responses are usually sharp in free metal nanoparticles [6]. In contrast, across the metal nanoparticle/dielectric interfaces of embedded nanoparticles, collective oscillations of electrons in metal nanoparticles are more relaxed due to the effect known as chemical interface damping [9]. In such cases, optical responses are quite broadened. In the case of matrix embedded metal nanoparticles, influence of the interface damping may be found out experimentally from the width of the SPR absorption. Excitation of quadrupolar modes of collective oscillations are also probable in cases where sizes of metal nanoparticles are of the order or more than the wavelength of light [6]. Optical responses due to the quadrupolar modes have been experimentally observed; for example, in the case of larger Ag nanoparticles in different glasses [10, 11]. Such nanoscale materials are found to be important for use in diverse applications like surface-enhanced Raman scattering [12], optical biosensors [13, 14], solar cells [15], all-optical logic gates [16], plasmonic waveguides [17] etc.

Analogous to the characteristic surface-plasmon resonance in pure metal nanoparticles, bimetallic alloy nanoparticles composed of noble metals (such as, Ag and Cu or Ag and Au) exhibit exciting optical responses [18, 19]. Interestingly, the optical responses are tunable from the ultraviolet to the infrared range of light wavelength, and the responses depend on metals and chemical compositions of metals in the alloy nanoparticles [20, 21]. Enhancement of local electric field at the surface-plasmon resonance frequency of the bimetallic alloy nanoparticles may be exploited to explore, for example, electron-phonon coupling in alloy nanomaterials of interest. In this regard, experimental and theoretical studies have been performed for pure cobalt and silver metal nanoparticles [22, 23]. For example, surface-confined acoustic vibration modes of semiconductor or metal nanoparticles are observed in the low-frequency Raman spectra of nanomaterials [24, 25]. Acoustic vibrations confined on the surface of nanoparticles, studied by the low-frequency Raman scattering, explain electron-phonon coupling in the nanoscale metal particles of interest. It would be interesting to explore nature of coupling phenomenon of this sort in bimetallic alloy nanoparticles also.

Compared to single pure metal nanoparticles, synthesis of bimetallic alloy nanoparticles composed of metals with different physical and chemical properties may be very interesting from basic understanding and can pave a way to design metamaterials suitable for various applications like colored glasses [26], photovoltaics [27], catalysis [28] etc. Scientific understanding of alloying of bulk metals and forming a solid solution is known for long time since the research studies of William Hume-Rothery in 1926. However, studies on alloy metal nanoparticles are quite recent. Synthesis of alloy metal nanoparticles of Ag and Cu, for example, is difficult through equilibrium processes due to huge mismatch (~14%) in the lattice parameters. However, using a non-equilibrium method like ion-beam induced sputtering, solubility limit of immiscible systems may be overcome. The method is also used to study response of materials in far from equilibrium conditions. Low-energy ion-beam sputtering technique is adapted and designed successfully to prepare the alloy nanoparticles composed of Ag and Cu or Ag and Au metals. Ion-beam induced sputtering and mixing of metallic elements at the nanoscale to obtain alloy nanoparticles with fine-tuned optical and structural...
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Ag-Ag$_2$O in a soda-lime glass matrix [29]. These samples were nanoparticles as well as core-shell hybrid nanostructures of photoluminescence properties of various nanomaterials. Almost continuous energy levels, very close to the edge of the conduction band of the semiconductor, form due to the excitons [8]. Formation of hybridized or coupled quantum states with plasmons (termed as plexcitons) in nanocomposite materials has been proposed [36]. Interactions of plasmons and excitons in the strong and weak coupling regimes have been studied in various hybrid nanomaterials in the recent past [37, 38]. These research studies hold a promising potential to elucidate the coupling phenomena in such novel optoelectronic materials.

This article presents a review about current studies on selected bimetallic alloy nanoparticles and metal-semiconductor nanocomposite materials, highlighting controlled tuning of optical responses and interesting photoluminescence properties of various nanomaterials.

Experimental Details

Materials processing

Bimetallic Ag-Cu or Ag-Au alloy nanoparticles were prepared using the ion-beam sputtering (IBS) technique. Low-energy Argon ions from the 150 kV particle accelerator were used to sputter the metal targets simultaneously. Sputtered metal atoms collected on a silica-glass have formed the alloy metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18]. For metal-semiconductor nanocomposite materials, molten-salt bath based ion-exchange method followed by 1 hr isochronal annealing at different temperatures (up to 600 °C) in vacuum (~1x10$^{-6}$ mbar) was used to synthesize silver metal nanoparticles. More details may be found elsewhere [18].

Characterization techniques

Avantes and Shimadzu dual-beam spectrophotometer (Model: PC 3101) was used to measure the optical responses of nanomaterials in the uv-visible wavelength range of light. Grazing incidence X-ray diffraction (GIXRD) measurements was carried out using Inel Equinox 2000 system to identify phases and crystal structures of the nanomaterials. X-ray photoelectron spectroscopy (XPS) studies were carried out in an ultrahigh vacuum chamber (~1x10$^{-10}$ mbar) fitted with dual X-ray sources. Al K$_\alpha$ was used as the exciting source (1486.6 eV) of photoelectrons. Mg K$_\alpha$ X-ray source was used to acquire Auger spectra in the normal mode. A hemispherical analyzer was used to identify chemical states of elements present in samples. Photoluminescence (PL) spectroscopy studies were carried out to explore the optical and electronic properties of the pure, alloy metal nanoparticles and metal-semiconductor nanocomposites. For the PL measurements, 488 nm line of Ar-ion laser (Coherent) with 60 mW powers was used as the excitation source. Scattered light from samples was dispersed using a double monochromator (Spx 14018) and detected using a cooled photomultiplier tube (FW ITT 130) operated in the photon counting mode. High-resolution transmission electron microscopy (HRTEM) measurements were performed using LIBRA 200 Zeiss microscope to determine crystal structures and estimate sizes of various bimetallic alloy nanoparticles.

Results & Discussion

Bimetallic alloy nanoparticles

Ion-beam processing of alloy metal nanoparticles is discussed here among other non-equilibrium techniques. Controlled ion-beam induced sputtering process has led to the formation of bimetallic alloy nanoparticles of Ag-Cu, or Au-Ag metals, for instance. Different experimental (e.g., optical absorption spectroscopy and X-ray diffraction) results confirm the formation of alloy metal nanoparticles. As discussed in subsequent sections, surface-plasmon optical resonance positions and shifts of Bragg angles in the X-ray diffraction pattern particularly corroborate the results.

In these discussions, samples composed of Ag-Cu bimetallic alloy nanoparticles are named as ‘S’ and ‘L’ for the lowest and the highest concentration of Cu atoms, respectively. Recorded optical absorption spectra of samples (S, M and L) are displayed in figure 2A. From the optical absorption spectroscopy experiments, the SPR absorption peaks have been observed around 483, 520 and 572 nm for samples S, M and L, respectively. As we know, SPR absorption positions for pure Ag and Cu metal nanoparticles in a silica-glass are around 400 and 650 nm, respectively [5]. Hence, SPR positions observed in samples S, M and L suggest that Ag-Cu bimetallic alloy nanoparticles had formed. Position of the SPR absorption peak has shifted towards higher wavelengths with increasing amount of Cu-atoms in the Ag-Cu alloy metal nanoparticles (Figure 2A). The optical response for the bimetallic alloy nanoparticles is thus tunable in the wavelength range of 400 to 650 nm. Optical response of the nanoparticles depends on the alloy compositions of metals [21].

Using the similar experimental conditions of ion-beam induced sputtering process, Au-Ag alloy metal nanoparticles
have been prepared on a silica-glass substrate. The composition of bimetallic alloy nanoparticles in this case is tailored by varying the exposure area of striking Ar⁺ ion-beam on the Au and Ag metal foils. For a given extent of ion-beam exposure on the metallic foils, sizes of Au-Ag alloy nanoparticles is controlled by varying the Ar⁺ ion beam fluences. Formation of the bimetallic alloy nanoparticles is confirmed here from the optical absorption spectroscopy measurements. Recorded optical absorption spectra of Au-Ag alloy metal nanoparticles are shown in figure 2B. SPR absorption positions are observed at 400 and 550 nm in pure Ag and Au metal nanoparticles, respectively (Figure 2B). In the present study, as shown in figure 2B, SPR absorption positions around 450 and 500 nm are recorded for various ion-beam sputtered samples. Observed SPR absorption positions thus suggest the formation of Au-Ag bimetallic alloy nanoparticles in this case. Here, position of the optical absorption resonance is shifted from 450 to 500 nm as a result of change in the composition of the bimetallic alloy nanoparticles [40].

Mechanism of nanoalloying

During the experiments of simultaneous ion-beam sputtering of Ag and Cu metal foils, induced by 100 keV Ar⁺ ions, sputtered Ag and Cu atoms emerge with energy in the range of few hundreds of eV [41]. Energetic sputtered heavy atoms impinging on the surface of a substrate create primary knock-on atoms, recoils, displacement cascades and dissipate their kinetic energy. Such collective impacts on an insulating material (e.g., silica-glass) are likely to heat up locally (~few nm) and induce a ‘temperature spike’ [42]. The spike raises substrate temperature substantially in a confined region. As a result, a molten transient state is created and intermixing of sputtered metallic atoms takes place on or in the sub-surface region of the substrate regardless of thermodynamic properties of the materials concerned. Thus, formations of metastable phases occur with the help of the temperature spike induced by the incoming energetic heavy ions. As lifetime of a thermal spike is of the order of few picoseconds, metastable phases are expected to quench fast and adopt possible stable structures [43].

Further, to continue the discussion on the ion-beam sputter deposited bimetallic alloy nanoparticles on a silica-glass, GIXRD patterns of Ag-Cu samples on a silica-glass are shown in figure 3. Dashed-lines (in black) correspond to diffraction peaks of bulk Ag (1 1 1), Ag (2 0 0) and the orange line shows Cu (1 1 1) diffraction peak in bulk Cu samples. In alloy nanoparticles of Ag-Cu metals, for example, X-ray diffraction peaks corresponding to Ag gradually shift towards higher Bragg angles (20 values) and the diffraction peaks corresponding to Cu marginally shift towards lower 20 values for samples with higher concentration of Cu atoms (Figure 3). As atomic size of Cu is lesser than Ag by ~12%, Cu atoms are likely to replace a fraction of Ag atoms in the crystalline lattice structure of Ag during the processing of Ag-Cu bimetallic alloy nanoparticles. As a result, lattice contraction of Ag crystals may take place. With the shrinkage of lattice spacing, the Bragg’s law of X-ray diffraction prescribes the Ag diffraction peaks to shift to higher 20 values and Cu diffraction peaks to move to lower 20 values. Marginal shifts are observed here for the Cu peak positions (Figure 3). Results of the X-ray diffraction studies are listed in table 1. Ag (1 1 1) X-ray diffraction peak positions (20) are observed at 38.8, 38.9 and 39.1° for samples S, M and L, respectively. For the bulk Ag
sample, the diffraction peak position for Ag (1 1 1) is at 38.0°. Large shifts of 20 values are found for Ag-Cu bimetallic alloy nanoparticles compared to the pure Ag metal.

$$\text{Table 1: GIXRD results of Ag-Cu bimetallic alloy nanoparticles [19].}$$

<table>
<thead>
<tr>
<th>Alloy samples</th>
<th>Ag (111) diffraction positions (2θ, in deg)</th>
<th>Lattice parameter (Å)</th>
<th>FWHM (rad)</th>
<th>Sizes of alloy nanoparticles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>39.1</td>
<td>3.985</td>
<td>0.0045</td>
<td>32</td>
</tr>
<tr>
<td>M</td>
<td>38.9</td>
<td>4.005</td>
<td>0.0065</td>
<td>23</td>
</tr>
<tr>
<td>S</td>
<td>38.8</td>
<td>4.015</td>
<td>0.0086</td>
<td>17</td>
</tr>
</tbody>
</table>

Scherrer formula (Equ 1) is used to calculate average sizes (R) of the Ag-Cu bimetallic alloy nanoparticles in samples S, M and L.

$$R = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{……………………………(1)}$$

In Equ 1, $\beta$ is the full-width at half maximum (expressed in radian) of Bragg diffraction peak, 2θ is the Bragg angle and $\lambda$ being the wavelength of Cu Kα line (1.54 Å). Sizes of the Ag-Cu alloy nanoparticles for samples S, M and L work out to be 17, 23 and 32 nm, respectively (Table 1). It may be noted that sizes of the alloy nanoparticles have increased with the increase of concentration of sputtered Cu atoms in samples S to L, respectively. Increase in average sizes of the bimetallic alloy nanoparticles with increase in Cu concentration is likely due to higher sputter-deposition of Cu atoms as well as due to faster diffusion of smaller Cu atoms. Average sizes of the Ag-Cu alloy metal nanoparticles, estimated from the HRTEM measurements (Figure 4) and the X-ray diffraction results (Equation 1) conform very well.

Compositions and sizes of bimetallic alloy nanoparticles thus synthesized following the ion-beam induced sputtering process and thermal mixing of metals may be compared. Details of thermal processing are not discussed here. However, it is found that ion-beam sputtering technique is much more effective to control compositions of the alloys and tailor sizes of the bimetallic alloy nanoparticles compared to thermal mixing [19]. It may be said, the ion-beam sputtering approach followed here with examples of Ag-Cu or Au-Ag bimetallic systems would enable to process alloy nanoparticles of other poorly miscible metals (e.g., Ni-Au) as well. Supported Ni-Au alloy nanoparticles are known as robust system for catalytic activities [44]. Growth and sintering behavior of Ni-Au bimetallic alloy nanoparticles supported on CeO (1 1 1) have been studied recently to understand catalytic reactions of the nanomaterials [45].

Metal-semiconductor nanocomposites

In the subsequent sections, discussions have been made to elucidate some interesting experimental results obtained in the metal-semiconductor nanocomposite samples. In this class of materials, encapsulation of Ag metal nanoparticles, for example, in different metal-oxide semiconducting compounds (AgO, AgCuO$_2$, or Ag$_3$O) exhibit very exciting optical and electronic properties.

**Ag-AgO**

Growth of Ag nanoparticles

As mentioned before, silver-sodium ion-exchange (Ag$^+$$\leftrightarrow$Na$^+$) method followed by thermal annealing in vacuum was used to prepare the composite nanostructures of Ag-AgO in a soda-lime glass. At the onset of the ion-exchange process around 320 °C, nucleation of fine particles of Ag atoms may take place due to thermal fluctuations in the local concentrations of diffusing Ag reactants (ions/atoms) [46]. Noble metals form a supersaturated solid solution due to their low solubility in glass matrices. Growth of the nucleated particles is expected by the diffusion of reactants to the surface of the stable nuclei. In the regime of diffusion-controlled-growth of spherical particles, average size of the particle increases with time $t$ is given by [47, 48]:

$$d^2(t) = d_0^2 + \frac{8}{\pi^2}C_s - C_p - C_e - D t \quad \text{………………………(2)}$$

where $d_0$ is the value of particle size at $t = 0$ (i.e., prior to growth), $C_r$ is the concentration of limiting reactant in the particle and $D$ is the diffusion coefficient of the limiting reactant. $C_s$ and $C_e$ are the concentrations of limiting reactants prior to growth and the equilibrium concentration in the matrix, respectively. The degree of supersaturation $C_r/C_e$ decreases during this stage of accretion. In the later stage of growth process when degree of supersaturation becomes negligible, coarsening (where larger particles continue to grow at the expense of smaller ones) takes place. In the present experimental condition, system may be on the early stage of growth because of the possible diffusion and reduction processes of available silver ions. The very supply of C$_s$ maintains the degree of supersaturation in the system and this could also prohibit coarsening to be effective within the time of annealing treatments of 1 hr.

Photographic images and optical absorption spectra are shown here (Figure 5) for the Ag ion-exchanged soda-lime glass samples, before and after vacuum annealing at different temperatures. Remarkable color changes (Figure 5A) have taken place with increasing annealing temperature up to 550 °C. Change of color observed is attributed to an increase of optical absorbance in these samples. The qualitative observation is complemented very well with the optical absorption spectroscopy experiments. For instance, observed increase of optical absorbance around 420 nm and concomitant
reduction of bandwidth of the surface-plasmon resonance absorption with the increase of annealing temperature confirms thermal growth of Ag nanoparticles in the soda-lime glass matrix (Figure 5B). As discussed before, in the present case growth of the Ag nanoparticles happens directly from the supersaturation, and the growth formula is provided in Equ 2. By measuring sizes of Ag nanoparticles after the isochronal annealing at various temperatures, activation energy for the diffusion of the silver ions in a soda-lime glass may be estimated using Equ 2. Details of such measurements are not discussed here, however, may be found elsewhere [46]. It may also be interesting to examine further mechanism and interrelation between the growth of the Ag nanoparticles and possible thermochemical transformation of the silver ion-exchanged soda-lime glass samples during the vacuum (i.e., neutral atmosphere) annealing. Depending on temperature of annealing and oxidation state of silver, chemical transformations in this case are quite likely. This would be elaborated in detail while discussing results of electron spectroscopy experiments performed on these samples.

PL results

Thermochemical transformation vis-à-vis thermal stability and corresponding changes in optical, electronic and chemical properties of the silver ion-exchanged soda-lime glass samples as a function of annealing temperature is of great interest from fundamental understanding as well as for technological importance. It will be shown, depending on the thermal history, silver could be in different oxidation states in the ion-exchanged soda-lime glass samples and the state of silver played a crucial role in governing optical and electronic responses of the nanomaterials. Primary results of photoluminescence (PL) spectroscopy measurements are discussed here. PL spectra of the silver ion-exchanged soda-lime glass samples and after annealing the samples in vacuum at different temperatures is displayed in the figure 6. Interestingly, substantial changes of the PL behavior are observed on annealing (Figure 6). For instance, here PL intensity reaches the maximum and sharply falls to the minimum value upon annealing at 450 and 600 °C, respectively. Reduction of the spectral intensity on annealing around these temperature ranges may occur as a consequence of thermochemical transformations of the nanomaterials. So, it becomes very pertinent to know about the chemical structures of materials at every stage of annealing. However, obtaining chemical information of these samples from the PL spectroscopy is unlikely. Hence, to obtain information about chemical changes of the nanomaterials with increasing annealing temperature, electron spectroscopy measurements have been performed to find out chemical states of silver in these samples. Explanations for the drastic reduction or quenching of the PL intensity are provided here with the help of other experimental results (e.g., X-ray photoelectron spectroscopy and uv-visible optical absorption spectroscopy).

Chemical phase study

Before proceeding to find out the origin of PL in these samples and elucidate observed quenching of the PL intensity in samples annealed at high temperatures, it is imperative to analyze first the X-ray photoelectron spectroscopy results. Figure 7 shows characteristic X-ray photoelectron (Ag 3d) and
Auger (MNN) spectra for silver in the silver-exchanged and annealed samples. Results from the X-ray photoelectron and Auger electron spectroscopy experiments reveal chemical states of silver in the ion-exchanged soda-lime glass samples before and after the annealing [29]. It may be important to know that chemical analysis of elements from X-ray photoelectron spectroscopy results only may be insufficient in some cases. Particularly, in case of silver, shift in electronic binding energies due to chemical reactions are comparable or less to that of the instrument resolution. In this case, calculations of modified Auger parameter further confirm chemical states of silver in these samples. Modified Auger parameter, $\alpha$ is defined as the sum of the binding energy of prominent photoelectrons and the kinetic energy of prominent Auger electrons of an element. The parameter is a good characteristic of the chemical states of the element concerned. Binding energy values of Ag$_{3d_{5/2}}$ photoelectrons and Modified Auger parameters for different samples are listed in table 2. Estimated value of $\alpha$ is 724.9 eV in the silver-exchanged soda-lime glass sample and it agrees very well with the reported data (724.8 eV) for the silver monoxide (AgO) phase. Chemical phase of the material is thus identified as AgO in the sample. Further, as shown in table 2, with reference to bulk Ag, shift in the Auger parameter values for silver in AgO and pure Ag$_2$O powders are 1.3 and 2.1 eV, respectively. These shifts are much higher compared to the binding energy shifts (~0.4 eV, see Table 2), providing more confidences in identifying chemical phases of these compounds. In thermally annealed samples, similar analyses confirm the existence of two chemical phases, pure Ag and Ag$_2$O. X-ray photoelectron spectra are shown in figure 8. Analyzed results are listed in table 2. Near the surface, Ag$_2$O/Ag ratio remains comparable with increase of annealing temperature. However, this ratio has reduced drastically inside the glass matrix (Table 2 and Figure 8). It clearly shows significant increase of volume fractions of pure Ag in the soda-lime glass samples with increase of annealing temperatures. To understand the increase of volume fractions of pure Ag, routes of thermochemical transformations may be proposed here. Most likely, Ag$_2$O and Ag$_3$O oxides break down according to following chemical reactions during the thermal annealing:

$$3\text{Ag}_2\text{O} \rightarrow \text{Ag} + \text{Ag}_3\text{O} + \text{O}_2 \quad (\text{annealing temperatures } \leq 450 \text{ °C}) \quad (\text{R1})$$

$$2\text{Ag}_2\text{O} \rightarrow 4 \text{Ag} + \text{O}_2 \quad (\text{annealing temperatures } \geq 450 \text{ °C}) \quad (\text{R2})$$

These reactions in high vacuum release silver ions in large amounts within the glass matrix. Nucleated silver particles formed during the ion-exchange process may act as the nucleation sites. Hence, during the annealing, growth of these nucleated Ag particles is expected because of diffusion of silver species (atoms/ions) in the soda-lime glass matrix.

PL Quenching

It may be apt now to explain the origin of PL in these samples and discuss about the quenching of the PL intensity on annealing at high temperatures. Experimental and deconvoluted PL spectra of silver ion-exchanged soda-lime glass sample and after annealing the sample at different temperatures are plotted in figure 9. Dominant emissions peak at 2.15 eV along with the other less intense peak at 2.28 eV are observed in the silver as-exchanged soda-glass sample (Figure 9A). It may be noticed that sharp optical absorptions are also observed exactly at the same energy values (Figure 9B) as the emission energies. Hence, these radiative transitions are due to the excitons in the AgO semiconductor materials in this sample. Photoexcited electrons may undergo nonradiative thermal scattering processes before forming bound excitons (e-h pairs). Excitons are confined in space by the Coulomb force and have enhanced probability to recombine radiatively providing light emissions and interesting information about their energy, band structures in semiconductors.

Photoluminescence behavior has changed completely upon annealing the silver-exchanged soda-glass sample. As shown in figure 9A, for instance, broad emission bands centered on 1.95 and 2.23 eV are displayed for samples annealed at 380 and 450 °C. Low-energy emissions around 2.0 eV are attributed to the presence of silver nanoparticles in the soda-lime glass samples and the emission centered on 2.23 eV is ascribed to the band-to-band radiative transition.
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In Ag$_2$O semiconductor materials [49]. Explanation for the quenching of PL intensity is given below: as mentioned before, with the increase of annealing temperature (up to ≤ 450 °C), silver may be released in the matrix as a result of thermal decomposition of AgO (R1). The chemical, AgO formed in the silver-exchanged soda-glass sample is unstable against heating and the material decomposes into Ag$_2$O and Ag during annealing in vacuum. As a result of this thermochemical reaction, volume fractions of Ag nanoparticles as well as Ag$_2$O increases. Presence of these chemicals are confirmed by the X-ray photoelectron and Auger spectroscopy measurements (Figure 8). Silver oxide (Ag$_2$O) phase is thermodynamically more stable structure compared to AgO. Also, being a direct band-gap semiconductor material, Ag$_2$O is highly photoluminescent. Thus, increased amount of the Ag$_2$O causes the PL intensity to reach the highest level around 450 °C. However, around this temperature, Ag$_2$O is again unstable and thermally decomposes according to the chemical reaction R2. Thus, the thermal decomposition of Ag$_2$O and substantial growth of silver nanoparticles simultaneously have resulted in the drastic quenching of the PL intensity observed for the samples annealed at 550 and 600 °C (Figure 6).

**Nanoparticles of Ag in AgCuO$_2$**

Among various mixed-oxide semiconductors, AgCuO$_2$ is found to be a new type of solar-energy semiconductor material. In most of the previous research studies, the AgCuO$_2$ material has been prepared using different chemical routes. A few of the synthesis methods may be described in brief. For example, i) AgCuO$_2$ precipitated out from the saturated aqueous solutions of AgNO$_3$ and Cu(NO$_3$)$_2$, while adding a solution of KOH and aqueous K$_2$S$_2$O$_8$ at 90 °C. Filtered precipitate was washed with deionized water, and dried in air at 70 °C [50], ii) aqueous solutions of equal volumes of copper acetate (Cu(CH$_3$COO)$_2$) and silver acetate (Ag(CH$_3$COO)) were separately prepared and then mixed. Aqueous NaOH was prepared separately with twice the concentration containing small amount of K$_2$S$_2$O$_8$ as an oxidizer. This alkaline persulfate solution was then slowly added to the metal acetate solution with stirring. The whole solution turned black indicating the formation of material in suspension [51], iii) AgCuO$_2$ nanoplates were electrodeposited onto indium-tin oxide (ITO) coated glass substrates near room temperature in an alkaline aqueous solution contained Ag(I)/Cu(II) ammonia complexes. The Ag(I)/Cu(II) ammonia complexes acted as water or ammonia oxidation catalysts to generate acid and lower the local pH at ITO electrode, and then Ag$^+$ and Cu$^{2+}$ ions were partially oxidized and dissociated from complexes to react with OH$^-$ to form AgCuO$_2$ deposits on the ITO coated glass substrates.

### Table 2: Finding chemical state of silver from the XPS studies [29].

<table>
<thead>
<tr>
<th>Sample history</th>
<th>BE (FWHM) of Ag$<em>3$d$</em>{5/2}$ (eV)</th>
<th>Deconvoluted BE (FWHM) (eV)</th>
<th>Modified Auger parameter $\alpha$ (eV)</th>
<th>Chemical compositions of Ag</th>
<th>Composition ratio of Ag$_2$O/Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk silver</td>
<td>368.4 (1.1)</td>
<td>-</td>
<td>726.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Ag$_2$O powders</td>
<td>367.8 (1.2)</td>
<td>-</td>
<td>724.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silver-exchanged</td>
<td>367.5 (1.3)</td>
<td>-</td>
<td>724.9</td>
<td>Ag$_2$O</td>
<td>Ag</td>
</tr>
<tr>
<td>450 °C annealed</td>
<td>367.9 (1.6)</td>
<td>367.8 (1.3)</td>
<td>-</td>
<td>Ag$_2$O</td>
<td>2.7</td>
</tr>
<tr>
<td>600 °C annealed</td>
<td>367.8 (1.6)</td>
<td>367.9 (1.3)</td>
<td>725.6</td>
<td>Ag$_2$O</td>
<td>2.4</td>
</tr>
<tr>
<td>550 °C annealed &amp; polished</td>
<td>368.3 (1.9)</td>
<td>367.9 (1.3)</td>
<td>726.0</td>
<td>Ag$_2$O</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 9: (A) Origin of PL from samples is explained (B) excitonic absorptions in silver-exchanged sample [29].
Various forms of oxides like CuO, AgCuO₂. Oxide phases undergo chemical changes on annealing in open air and resulted in a decrease in the intensity of absorption modes. These experimental results suggest that most of the Ag nanoparticles had undergone chemical changes on annealing in open air and resulted in a decrease in the intensity of absorption modes. Upon annealing the bilayer sample at 500 °C for 1 hr, in fact, all the absorbance peaks have disappeared. These experimental results indicate the formation of Ag particles in this case may be due to the formation of Ag-Cu alloys as well as the growth of various oxide phases. Moreover, upon annealing at 500 °C, the diffraction peak intensity at 36.5° corresponding to AgCuO₂ (111) phase has become relatively strong, indicating growth of the particular oxide phase around this temperature.

As mentioned before, samples (Ag nanoparticles in the AgCuO₂ semiconductor) have been synthesized by annealing Ag/Cu bilayer thin films on a silica glass at various temperatures in an open ambient air for an hour. Optical absorption spectra recorded in these samples are displayed in Figure 10. As shown, leading dipolar SPR absorption centered on 425 nm with a broad bandwidth is observed upon annealing the Ag/Cu bilayer thin film sample at 300 °C. Smaller Ag nanoparticles are known to produce broad SPR bandwidth in optical absorption spectra. Along with the dipolar SPR response, another less intense optical absorption peak around 340 nm is also observed. This particular spectral feature is characteristic of the quadrupolar mode of collective oscillations in larger Ag nanoparticles. Few previous research studies have discussed the presence of quadrupolar mode in metal nanoparticles of sizes 50 nm and above. For particle sizes (R) where R << λ (λ being the wavelength of light), dipolar SPR absorption is dominant compared to higher absorption modes (e.g., quadrupole). Depending on sizes of metal nanoparticles, collective oscillations of free electrons may give rise to both the absorption modes. Results from the present optical absorption spectroscopy studies indicate the formation of Ag nanoparticles of various sizes (approximate range of 5 to 50 nm) in the Ag/Cu bilayer samples upon thermal annealing at 300 °C. Formation of Ag nanoparticles in this case may be occurring due to thermal dewetting. Also, precipitation of Ag atoms is preferred due to low thermal miscibility between Ag and Cu metals and poorer chemical activity of Ag with O atoms compared to that of Cu atoms.

Further, as shown, intensity of optical absorptions in the Ag/Cu bilayer sample is reduced significantly on annealing at higher temperatures. For example, the dipolar optical response is weakened notably for the sample annealed at 400 °C and the quadrupolar mode (observed at 300 °C) is blue-shifted. Upon annealing the bilayer sample at 500 °C for 1 hr, in fact, all the spectral features have disappeared. These experimental results suggest that most of the Ag nanoparticles had undergone chemical changes on annealing in open air and resulted in various forms of oxides like CuO, AgCuO₂. Oxide phases have been identified here from the X-ray diffraction results. Due to enhanced thermo-chemical activities at the nanoscale dimensions, metal nanoparticles are susceptible to oxidation upon annealing at higher temperatures in ambient air. Thermal mixing and coalescence of metal nanoparticles due to annealing at 500 °C may give rise to the observed featureless optical absorption spectra in the sample. Details are not presented here, but experimental results from Rutherford backscattering studies do confirm thermal mixing of bimetallic layers on annealing at higher temperatures.

GIXRD patterns of as-deposited and thermally annealed samples of Ag/Cu bilayer thin films on silica-glass substrates are displayed in Figure 11. Dotted lines show the X-ray diffraction peaks corresponding to Ag and Cu in the as-deposited sample. A new diffraction peak appears at 36.5° on annealing at 300 °C. This indicates the formation of AgCuO₂ (111) phase. Further, it may be noted that all the Ag and Cu diffraction peaks have shifted towards higher 2θ values on annealing at 300 and 400 °C (Figure 11). The shift is marginal in samples annealed at 300 °C. Considerable shifts, about 1°, corresponding to Ag diffraction peaks have been observed for samples annealed at 400 °C. Shifts are ascribed to the formation of Ag-Cu alloys as well as growth of various oxide phases. Moreover, upon annealing at 400 °C, the diffraction peak intensity at 36.5° corresponding to AgCuO₂ (111) plane has become relatively strong, indicating growth of the particular oxide phase around this temperature.

It may also be seen that the intensity of Cu (1 1 1) diffraction plane was reduced significantly on annealing at higher temperatures for example, the dipolar optical response is weakened notably for the sample annealed at 400 °C and the quadrupolar mode (observed at 300 °C) is blue-shifted. Upon annealing the bilayer sample at 500 °C for 1 hr, in fact, all the spectral features have disappeared. These experimental results suggest that most of the Ag nanoparticles had undergone chemical changes on annealing in open air and resulted in various forms of oxides like CuO, AgCuO₂. Oxide phases have been identified here from the X-ray diffraction results. Due to enhanced thermo-chemical activities at the nanoscale dimensions, metal nanoparticles are susceptible to oxidation upon annealing at higher temperatures in ambient air. Thermal mixing and coalescence of metal nanoparticles due to annealing at 500 °C may give rise to the observed featureless optical absorption spectra in the sample. Details are not presented here, but experimental results from Rutherford backscattering studies do confirm thermal mixing of bimetallic layers on annealing at higher temperatures.

![Figure 10: Optical absorption intensity is reduced drastically upon annealing the metal films on silica-glass substrates](image-url)
decomposed due to the given heat treatment according to following thermo-chemical reaction:

\[ 2\text{AgCuO}_2 \rightarrow 2\text{CuO} + 2\text{Ag} + \text{O}_2 \quad \text{(R3)} \]

The decomposition reaction released copious amount of Ag atoms into the matrix. Moreover, a new peak corresponding to CuO (200) diffraction plane at 38.7° appeared on annealing at 500 °C. The data also corroborated the decomposition reaction R3. Shift of X-ray diffraction peaks corresponding to Ag for the sample annealed at 500 °C was less compared to the samples annealed at 300 and 400 °C (Figure 11). This data provided an indication of the decomposition of AgCuO2 phase through which copious amounts of pure Ag atoms were released.

**Figures**

Figure 11: GIXRD patterns of metal films on silica-glass substrates, before and after thermal annealing [39].

**Summary**

Research potentials about various syntheses of nanomaterials, characterizations and their extraordinary physical (optical, structural, electronic etc.) and chemical properties at nanoscale dimensions have been discussed in this article. Most of the elaborated results are found to depend on compositions and sizes of the nanomaterials. Compared to pure metals, for example, bimetallic alloy nanoparticles exhibit controlled tuning of optical responses over a broad wavelength range. This fact is interesting from different perspectives. Exciting quasi-particle interactions among plasmons and excitons along with interesting photoluminescence and chemical properties of metal-semiconductor nanocomposite materials have been elucidated. In addition to basic understanding of phenomena at reduced dimensions, the nanomaterials are potential candidates for future novel optoelectronic applications.

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**References**


