In situ real time optical study of films grown on low temperature substrates by vacuum evaporation of iodine and silver iodide: spectral transitions during deposition and annealing processes

In situ real time optical study of films grown on low temperature substrates by vacuum evaporation of iodine and silver iodide: spectral transitions during deposition and annealing processes

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Abstract

In order to clarify the growth process and hard to understand reported spectra of iodine film and silver iodide (AgI) film, various spectral transitions have been measured *in situ*: (a) optical density spectra of films grown on low temperature substrates by vacuum evaporation of an iodine lump, during deposition and annealing; (b) optical extinction spectra of vapour zones produced by gas evaporation of AgI powder, during evaporation; and (c) optical density spectra of films grown on low temperature and room temperature substrates by vacuum evaporation of AgI powder, during deposition and annealing. After these *in situ* real time measurements, the film specimens were allowed to recover and were examined by means of comparative measurements of the optical density and photoluminescence spectra at about 12 K. The spectra obtained were analysed and compared with those reported previously by other workers, and the following questions have been optically clarified: (1) How does annealing improve the crystal quality of iodine film? (The annealing at about 200 K improves the crystal quality considerably.) (2) What is the film that is quench deposited on low temperature sapphire surfaces by thermal evaporation of AgI powder? (It is $Ag_m I_n$ ($m, n \geqslant 1$) dispersed iodine film.) (3) How does AgI film grow in the deposited film? (Above about 220 K, iodine evaporates abruptly to grow uniform AgI film on the substrate.) (4) How does excess iodine affect the optical spectrum of AgI? (The excess iodine creates both several exciton absorptions due to polytype structures at wavelengths between 370 and 410 nm, and a tail at wavelengths longer than 430 nm.) (5) What is the best evaporation condition for the fabrication of AgI and iodine films? (The best quality of iodine and βAgI films can be obtained at a substrate temperature of about

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200 K in the quench deposition method.) Besides this, the present optical
experiments have answered the following question: is there truly a strongly
enhanced optical absorption in quench deposited AgI films, as reported by
Kondo *et al* (1998 *Phys. Rev.* B **57** 13235)? The present studies have elucidated
that the enhanced absorption is not due to amorphization of AgI but due merely
to intense optical absorption of iodine in the films.

1. Introduction

Because of the practical importance of silver iodide, AgI, in electrolytes, photography and
cloud condensation nuclei, the physical and chemical properties have been extensively studied
in the last few years. AgI has three phases designated as α, β and γ, in order of decreasing
temperature, at normal pressure with the following properties (Burley 1963). At the superionic
transition temperature T_c (420 K), the superionic α phase transforms into semiconductor β
phase (wurtzite lattice). The α phase has a body-centred cubic arrangement of I^- ions with
highly mobile Ag^+ ions randomly distributed through the equivalent interstices; this is known as
the averaged structure. At room temperature, the semiconductor γ phase (zinc-blende lattice)
appears as a metastable state. It is said that the stability of the γ phase is affected by slight
nonstoichiometries and other defects. To date, the optical spectra of pristine AgI (Cardona
1963, Mochizuki 2001, Mochizuki and Ohta 2000) and AgI nanoparticles (Mochizuki and
Umezawa 1997, Dulin 1993), AgI-based composites (Mochizuki and Fujishiro 2003a, 2003b)
and AgI-based glasses (Fujishiro and Mochizuki 2002, Mochizuki and Fujishiro 2003c) have
been reported, by many workers. However, it is well known that the AgI specimens tend
to contain excess iodine. The excess iodine species in real AgI specimens are thought to
be dependent on the specimen preparation method and thermal history. Iodine clusters I_n
($n > 2$) and films exhibit several intense broad optical absorption bands in the visible and
ultraviolet light regions. Although such excess iodine effects have not been reported in detail,
we have frequently experienced these absorption bands due to excess iodine disappearing
or weakening considerably upon annealing at moderate temperature in vacuum, and found
that βAgI film with high optical quality is fabricated by both depositing and subsequently
annealing below room temperature. For example, although excess iodine in film specimens is
stable at low temperatures ($T < 90$ K) even in vacuum, it rapidly evaporates above about 220 K
under heating. Kondo *et al* (1998) prepared films on a low temperature sapphire substrate by
evaporating AgI in vacuum and observed extremely enhanced absorption compared to that of
crystalline AgI film; the enhanced absorption appearing in thick and thin films disappeared
suddenly at temperatures higher than 220 and 180 K, respectively. They explained the enhanced
absorption by the p–d hybridization in amorphous AgI and the disappearance of the intense
absorption by an amorphous–crystalline transition. However, we have found very recently that
such intense absorptions, spectral shapes and sudden spectral disappearances are very similar
to those observed for pristine iodine films. Unfortunately, these excess iodine effects have
been accorded too little respect in the optical study of AgI and AgI-based materials for a long
period of time and they have led many researchers astray.

In the present study, we have performed *in situ* real time measurements of the optical
spectra of AgI films and pristine iodine films deposited on the same low temperature sapphire
surfaces, during both deposition and heating (annealing) processes. Besides this, we have
measured optical extinction spectra of AgI vapour zones and have clarified the vapour species.
After these measurements, the AgI film specimens grown were examined by means of
comparative measurements of the optical density (OD) and photoluminescence (PL) spectra

at about 10 K. On the basis of these experimental results, we have studied the AgI film growth mechanism below room temperature and elucidated several AgI-related phenomena which were previously reported by other authors but were hard to understand.

2. Experimental procedure

Vacuum evaporation experiments were carried out under a base pressure below 10^{-4} Pa by using a stainless-steel evaporation chamber with two pairs of opposite optical windows. The experimental apparatus was composed of a main evaporation chamber and a spectral measurement system. The apparatus was used previously for cluster and microcrystal studies (Mochizuki 1996, Mochizuki and Ruppin 1993). Optically flat plates of sapphire (R-cut) were used as the substrate. The substrate temperature (T_s) was monitored with a copper–constantan thermocouple. For evaporation of AgI, a platinum crucible containing nominally pure AgI (Alpha, 99.999%) powder was gradually heated indirectly in an alumina crucible on which a tungsten wire heater was wound. The iodine vapour was obtained by evacuating a glass tube which contained nominally pure iodine lumps (Wako, 99.8%) and was connected to the evaporation chamber. In the present experiments, the thickness of film on the substrate increased with time. During the deposition, the OD spectrum of the selected position in the film was recorded as a function of time (t_d) elapsed after the beginning of the measurement with an optical multichannel analyser system. Each measurement was made at the appropriate time window and time interval. A time (t_d) resolved spectrum consists of 64 spectra. In the present paper, some of them are selected and presented. Continuum light from a 150 W xenon lamp was appropriately attenuated to avoid photoinduced blackening and was directed at the whole substrate in a transmission configuration without using a lens. After passing the substrate, only the light through the selected position was collected by a lens and then spectrally analysed and recorded by a multichannel analyser system (Atago, MAX 3000). The transmission T_r at a given position is the intensity ratio at the same position before the beginning of the evaporation. The results for films are expressed with respect to the OD spectra, $-\log T_r$.

Generally, the vapour produced by the vacuum evaporation method is too thin for usual optical absorption measurements and the vapour needs to be confined. In order to confine the vapour, the gas evaporation experiments on AgI were carried out at different gas pressures and the optical extinction spectra were measured at different stages of evaporation, using the apparatus described above to determine optically the vapour species in the AgI vapour, taking into account some aggregation of vapour species due to atmospheric gas. Optical extinction spectra of selected positions in the vapour zones were recorded in the transmission configuration as a function of t_d elapsed from the beginning of the measurement. Since the transmissivity spectra obtained for the vapour zones contain both scattering and absorption effects, the results obtained are expressed as optical extinction spectra, $-\log T_r$.

After the above-described *in situ* real time measurements, the recovered AgI film specimens were put in a helium closed-cycle cryostat, whose temperature could be varied from about 10 to 300 K. PL was excited by different laser lines (360–440 nm) from a Ti^{3+}:sapphire laser excited by a Nd^{3+}:YAG laser. The PL spectra were examined at different laser lines with different excitation intensities. The emitted light was dispersed using a grating spectrograph (Jobin-Yvon HR-320), and an image-intensified multichannel photodetection system (Lambda Vision, LVID) was employed. Both the OD spectra and the PL spectra were measured at about 10 K. The PL spectra were also measured at different temperatures between 7 K and room temperature. The spectral response of the optical system, including the focusing lens and the optical fibre, was carefully measured using a calibrated quartz–halogen lamp and used to correct the raw data. Through the above optical measurements, the lights from the xenon lamp and laser were suppressed to avoid photoblackening.
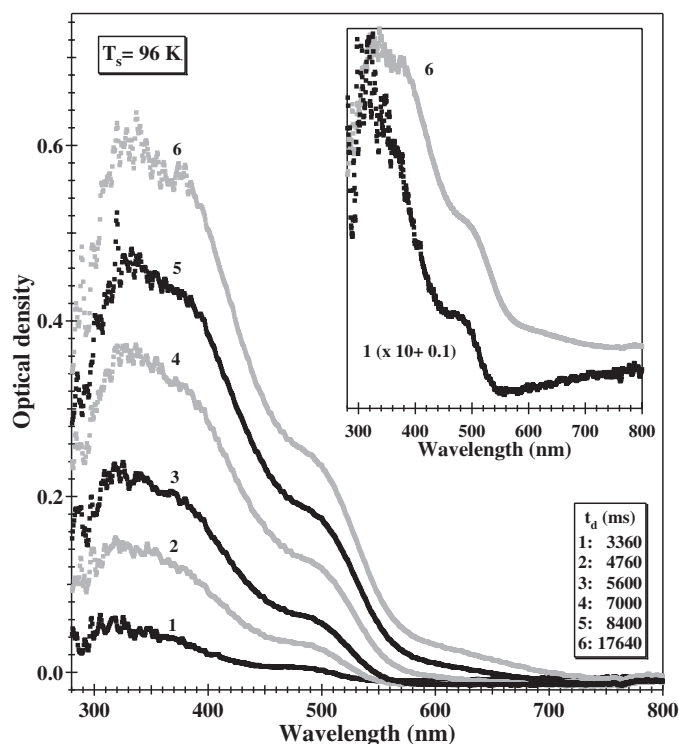
Figure 1. The time evolution of the optical density spectrum of iodine film on a sapphire substrate ($T_s = 96$ K) during deposition. The spectra at the initial and final stages of the deposition are compared in the inset.

3. Results and discussion

3.1. Time evolution of the optical density spectrum of iodine film deposited on a sapphire substrate during vacuum evaporation of pristine iodine

We evaporated iodine at different evaporation speeds and at different substrate temperatures. Figure 1 shows the time evolution of the OD spectrum of the iodine film deposited on a sapphire substrate whose temperature was 96 K, as a typical example. Each measurement was made for 140 ms at intervals of 140 ms. The time t_d increases for the curves from bottom to top. The time evolution corresponds to the film thickness increase. With increasing t_d, the absorption increases with the spectral broadening. Although the spectra at the transparent region (>600 nm) are affected by some interference effect, curve 1 can be compared with curve 6 by rescaling: $\times 10 + 0.1$. The spectra of iodine film obtained are very different from those of iodine molecules (Mathieson and Rees 1956). This indicates that the strong molecular interaction in solid iodine affects its electronic structure. The absorption of curve 6 starts to rise around about 760 nm, which is comparable to the reported bulk values deduced from optical and photoconduction measurements: 733 nm at 78 K and 779 nm at 200 K (Braner and Chen 1963), 775 nm at 123 K (Yamamoto *et al* 1987), 827 nm at 300 K (Many *et al* 1961), 992 nm at room temperature (Riggleman and Drickamer 1963) and 939 nm at room temperature (Moss 1952). The absorption rises gradually up to about 580 nm, and reaches an inflection point at about 580 nm. After reaching a kink at about 505 nm, the absorption rises steeply to another kink at about 380 nm. Passing through a maximum at about 320 nm, the absorption decreases
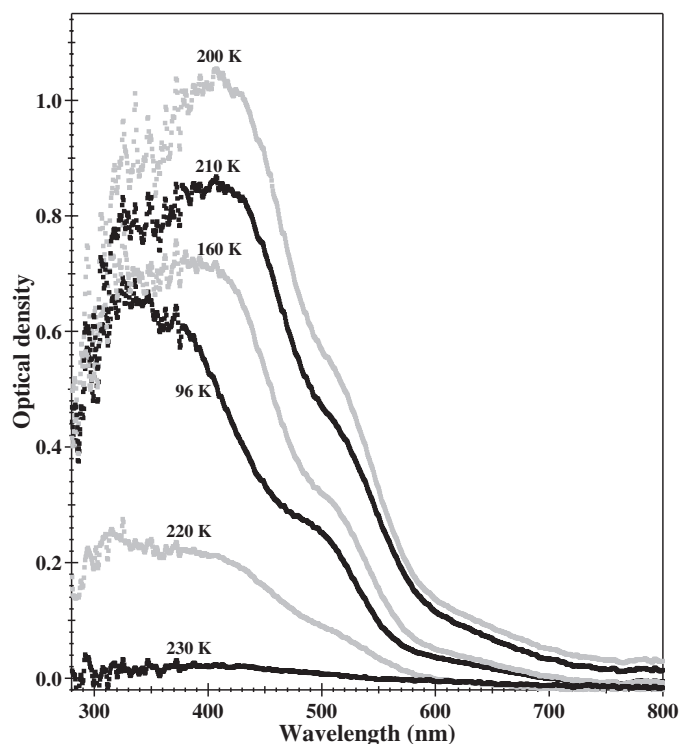
Figure 2. The temperature dependence of the optical density spectrum (curve 6 in figure 1) of iodine film on a sapphire substrate during heating.

steeply. We elevated the specimen temperature to room temperature and measured the spectra at different temperatures. The results are shown in figure 2. With increasing temperature, the absorption continues to increase and reaches a maximum at 200 K. On further increasing the temperature, the absorption decreases monotonically. When the temperature exceeded 220 K, there was a faint exhaust sound from the vacuum pump attached to the specimen chamber and the OD spectrum disappeared suddenly. Both the exhaust sound and the disappearance of the OD spectrum indicate perfect evaporation of the iodine film. Through different experiments, it was found that the spectral disappearance temperature tends to vary with heating rate and film thickness. The temperature dependence of the spectral structure is summarized as follows. The peak wavelength at about 320 nm is not changed with temperature increase. However, the absorption components corresponding to the kinks at about 505 and about 380 nm and to the inflection at about 580 nm shift toward longer wavelengths. The spectrum at 200 K seems to consist of at least three absorption bands centred at about 320, about 410, about 510 nm and a tail at wavelengths longer than 600 nm. They correspond to the 340.0, 411.0, 495.0, 537.0 and 602.5 nm absorption bands observed for iodine single-crystal films (Schnepp *et al* 1965). These five absorptions are assigned to optical transitions from valence bands originating from the π_g, π_u and σ_g orbits in I_2 molecules and to conduction bands originating from σ_u orbits in I_2 molecules (Yamamoto *et al* 1987, Schnepp *et al* 1965). It is known that the iodine films deposited at 123 K were polycrystals of orthorhombic structure (Grimminger and Richter 1956). It has been experimentally known that, when a substance of anisotropic crystal structure is evaporated onto a low temperature substrate, the film produced tends to contain a considerable number of defects. The present film was produced at temperature lower than
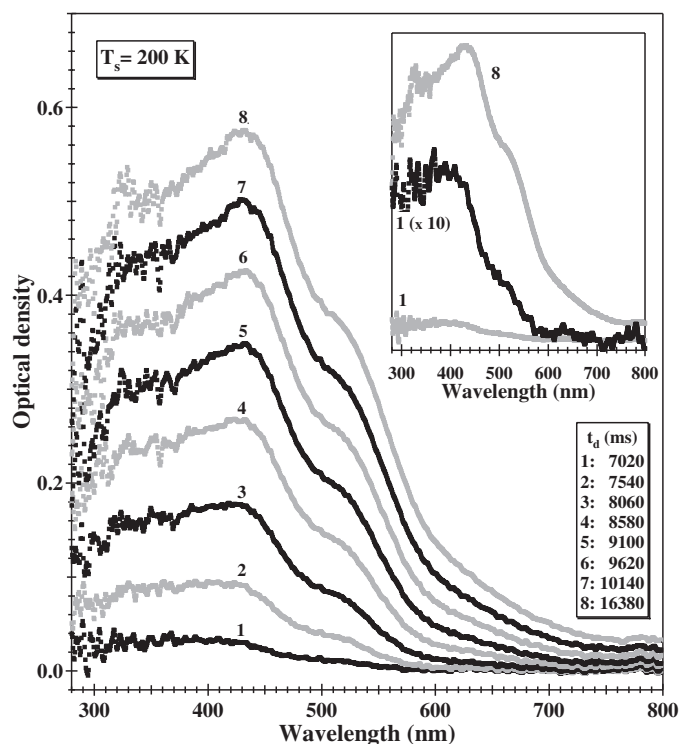
Figure 3. The time evolution of the optical density spectrum of iodine film on a sapphire substrate ($T_s = 200$ K) during deposition. The spectra at the initial and final stages of the deposition are compared in the inset.

123 K and therefore it may contain some crystal defects. The absorption intensity increase of these bands with increasing temperature from 96 to 200 K may arise from some improvement in crystal quality of the film upon thermal annealing. Therefore, we deposited iodine on a higher temperature substrate ($T_s > 96$ K) and measured the OD spectrum during deposition.

Figure 3 shows the time evolution of the OD spectrum of the iodine film deposited on a sapphire substrate whose temperature was 200 K, as a typical example. Each measurement was made for 130 ms at intervals of 130 ms. In the inset, curve 1 obtained at the initial stage is compared with that obtained at the final stage by rescaling curve 1. A shoulder appears at about 439 nm in an absorption tail (>415 nm) of some higher energy band which seems to consist of several bands. As the deposition progresses, two absorption bands appear at 331 and 435 nm, and at least two shoulder bands appear and become prominent at about 510 nm and below 600 nm. As the deposition progresses further, the absorption intensities of these bands and the shoulder bands increase. The spectral structure is similar to that of the iodine single-crystal film reported by Schnepp *et al* (1965). At the final stage of the deposition, the 331 and 435 nm bands become sharper. The 435 nm band is accompanied by some bands between 370 and 410 nm. After the deposition, the iodine film was cooled down to 96 K and then it was heated to room temperature. During the cooling and heating processes, the OD spectrum was measured as a function of temperature. The result is shown in figure 4. With temperature decreasing to 96 K, the 439 nm band becomes intense and sharp with an accompanying slight red-shift, while the 331 nm one is almost unchanged. The 510 nm shoulder becomes a clear absorption band at about 510 nm. The absorption slope at wavelengths longer than 600 nm grows into a shoulder.
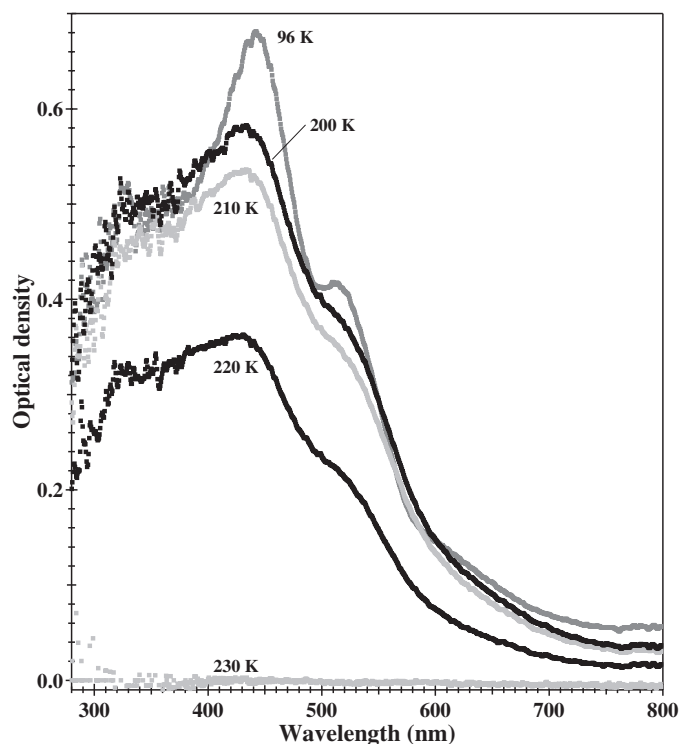
Figure 4. The temperature dependence of the optical density spectrum (curve 8 in figure 3) of iodine film on a sapphire substrate during heating.

With increasing temperature from 96 K, the absorption decreases monotonically. As for the film deposited at 96 K, when the temperature exceeded 220 K, we heard the faint exhaust sound and the OD spectrum disappeared suddenly. The spectral evolution shown in figures 1 and 3 may be explained by the spectral transition from island-like ultrathin film to uniform thick film. In the spectra (curves 1 in the figures) measured at the initial stage of the deposition, small numbers of I_2 molecules are thought to condense to form each island. In such cases, the spectrum tends to resemble that of free I_2 molecules and the apparent optical absorption edge shifts to shorter wavelengths, as shown in figures 1 and 3. The spectral evolution from molecule to solid, together with such an apparent red-shift of the absorption edge, has been explained by calculating electronic energy structures for I_2 and I_n ($n > 2$) (Satoko 2003). Calculation of stable structures of I_n in our laboratory is planned.

3.2. Time evolution of the optical extinction spectrum of vapour produced by thermal evaporation of pristine AgI in helium gas

Figure 5 shows a typical view of the gas evaporation of AgI in helium gas confined at 110 Torr. This photograph was taken at the middle stage of gas evaporation with illumination from a xenon lamp. A dark zone (DZ), ranging from the upper edge of the crucible to a height of about 5.2 mm, and a long conical brown smoky zone (BSZ) can be clearly distinguished. The smoky nature arises from light scattering by particles with sizes comparable to the incident light wavelength. This suggests that the species of the BSZ are large microcrystals. As the gas evaporation proceeds, the BSZ grows to produce a multilayer cone structure which consists of a brown inner zone and a blue outer zone. With decreasing helium gas pressure, the vapour
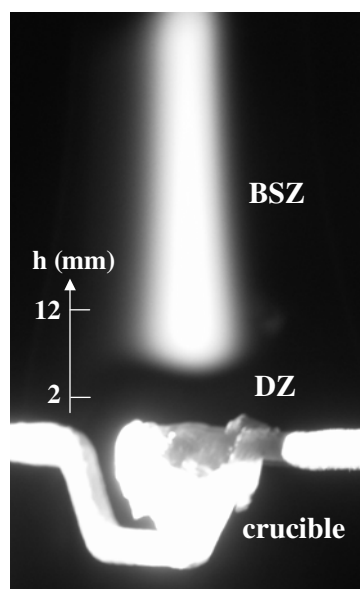
Figure 5. Vapour zones produced by thermal evaporation of AgI powder in He gas confined at 110 Torr. BSZ and DZ are the brown smoky zone and the dark zone, respectively.

zone structure becomes spread and indistinct. As a result, it becomes impossible to measure the extinction spectrum.

Figure 6 shows the time evolution of the optical extinction spectrum of the BSZ at a height of 12 mm from the crucible edge at 110 Torr. Each time t_d is given in the figure. At the initial stage of the gas evaporation, the observed spectrum (curve 2) consists of an absorption band P centred at about 510 nm and another absorption band Q increasing toward about 320 nm. With progressive evaporation, these bands grow as shown by curves 3, 4 and 5. The P band is assigned to the X–B electronic–vibrational transitions in iodine diatomic molecules I_2 (Yamamoto *et al* 1987), while the absorptions due to the X–B transition in isotopes of AgI molecules, ^{109}AgI and ^{107}AgI (Stueber *et al* 1998), and the interband transition in AgI microcrystals (Mochizuki and Umezawa 1997, Dulin 1993) appear in the Q-band wavelength region. In the inset, the optical extinction spectrum of the DZ at a height of 2 mm from the crucible edge is shown. This spectrum was obtained at the steady state of the gas evaporation. The absorption band centred at 515 nm and the absorption which increases toward 270 nm are assigned to the X–B and X–C electronic–vibrational transitions in I_2 molecules, respectively (Yamamoto *et al* 1987). Differing from the case for the gas evaporation of pristine silver (Mochizuki and Ruppin 1993), the absorption lines due to atomic silver Ag_1, the absorption bands due to silver diatomic molecules Ag_2 and silver particles Ag_n ($n > 2$), and the absorption due to the X–A transition in AgI molecules (Metropolis 1939) are not resolved clearly in the broad featureless spectra. However, the existence of silver vapour species is ascertained at the initial stage of the film formation on a substrate whose temperature is 200 K, as shown in the next subsection. Stueber *et al* (1998) already found isotopes of AgI molecules (^{109}AgI and ^{107}AgI) and Ag atoms as species in the molecular beam generated by expansion cooling of vapour which was produced by heating AgI. After the gas evaporation experiments, we found some residual substance in the crucible and thin yellow particles deposited on the upper lid of the evaporation chamber. We examined them by x-ray diffractometry and photoluminescence spectroscopy. The x-ray diffractogram showed that the residual substance in the crucible was silver metal and the thin
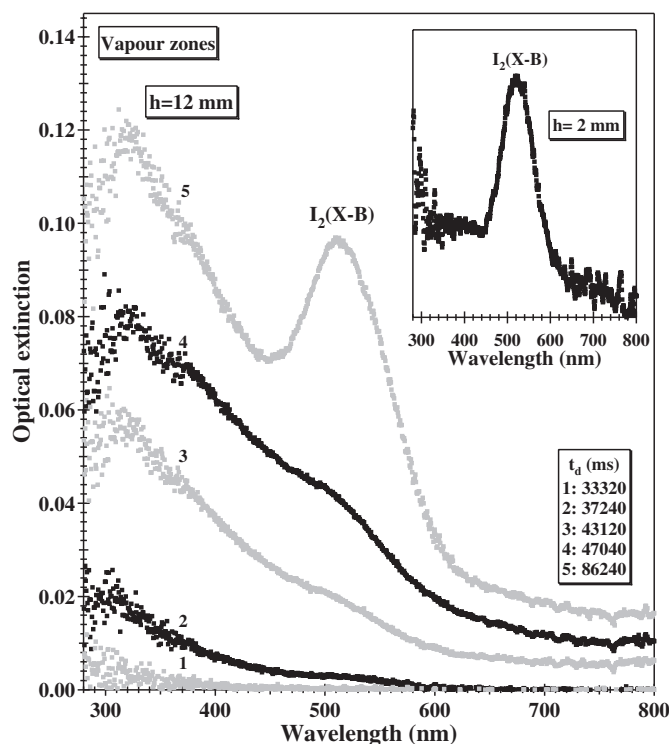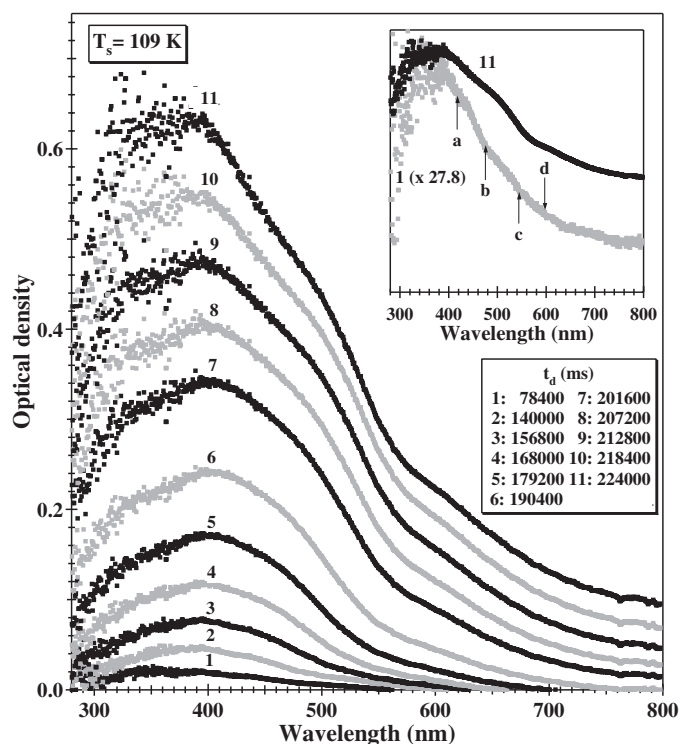
Figure 6. The time evolution of the optical extinction spectrum of the brown vapour zone at a height of 12 mm from the crucible edge during evaporation. The optical extinction spectrum of the dark vapour zone at a height of 2 mm from the crucible edge for the final stage of the gas evaporation is shown in the inset.

yellow deposits were mixtures of βAgI and γAgI microcrystals. Taking account of the vapour species aggregation promoted by atmospheric He gas, it is suggested that Ag_mI_n ($m, n \geqslant 1$) particles, I_2 molecules and Ag atoms may all be vapour species in vacuum evaporation. The chemical formula Ag_mI_n is the general term for AgI diatomic molecules, AgI clusters (($AgI)_n$) and nonstoichiometric silver iodide clusters (($AgI)_nAg_\delta$ ($\delta > 1$) and $(AgI)_nI_\varepsilon$ ($\varepsilon > 1$)). The $(AgI)_nAg_\delta$ and $(AgI)_nI_\varepsilon$ are known as fragment clusters. These vapour species from the crucible are deposited on the high temperature substrate to produce a film. When the substrate temperature is lower than 220 K, the vapour species adsorbed on the substrate may condense to form Ag_n–Ag_mI_n–I_2 composite film. Since the rate of evaporation of I_2 is higher than those for other species, Ag_n and Ag_mI_n are thought to be embedded in an iodine film matrix. This speculation may be ascertained spectroscopically, as reported in later subsections.

3.3. Time evolution of the optical density spectrum of film deposited on a low temperature substrate during vacuum evaporation of AgI

Figure 7 shows the time evolution of the OD spectrum of the film deposited on a sapphire substrate at 109 K during vacuum evaporation. Each measurement was made for 1600 ms at intervals of 4000 ms. In the inset, curve 1 obtained at the initial stage is compared with that obtained at the final stage by rescaling curve 1. The colour of the film was light brown. Although the spectra are broader than those of iodine films, faint inflection points (a, b, c and d) are seen at about 417, about 475, about 544 and about 597 nm at the initial stage of

Figure 7. The time evolution of the optical density spectrum of the film deposited on a sapphire substrate ($T_s = 109$ K) during vacuum evaporation of AgI powder. The spectra at the initial and final stages of the deposition are compared in the inset.

the evaporation. As compared with the absorption spectra of pristine AgI (Cardona 1963, Mochizuki and Ohta 2000, Mochizuki 2001) and pristine iodine films described above, the following are found. The inflection at 417 nm is due to the $Z_{1,2}$ exciton absorption (422 nm). The inflections at 475, 544 and 597 nm arise from the absorption bands centred at 340, 411, 495, 537 and 603 nm in iodine films. That is, the film on the low temperature substrate at the initial stage of the deposition is a composite film made of, at least, AgI and iodine. It is hard to deduce the absorptions due to other species from the observed spectra. With progressing deposition, the absorption increases and the absorption edge extends to wavelengths longer than 800 nm. One possible cause of such a spread in absorption is additional optical scattering at the I–AgI interfaces in the I–AgI composite specimen. We elevated the specimen temperature to room temperature and measured the spectra at different temperatures during heating. The results are shown in figures 8(a) and (b). With increasing temperature, the absorption continues to increase and then reaches a maximum at 210 K. The colour of the film becomes dark brown. On further increasing temperature, the absorption decreases monotonically. Similarly to in the above-described experiments for iodine films, when the temperature exceeded 230 K, there was the same exhaust sound. Simultaneously, the intense broad spectrum disappeared suddenly, a weak spectrum peculiar to AgI emerging. Both the exhaust sound and the spectral change indicate the evaporation of excess iodine from the film and indicate also that vapour species related to AgI evaporation are dispersed in an iodine film matrix. Through experiments under different conditions, it is found that the spectral change temperature tends to vary with heating speed and film thickness. With temperature increasing from 240 to 290 K, the tail at wavelengths longer than 430 nm becomes considerably weakened and the absorptions between 370 and 410 nm
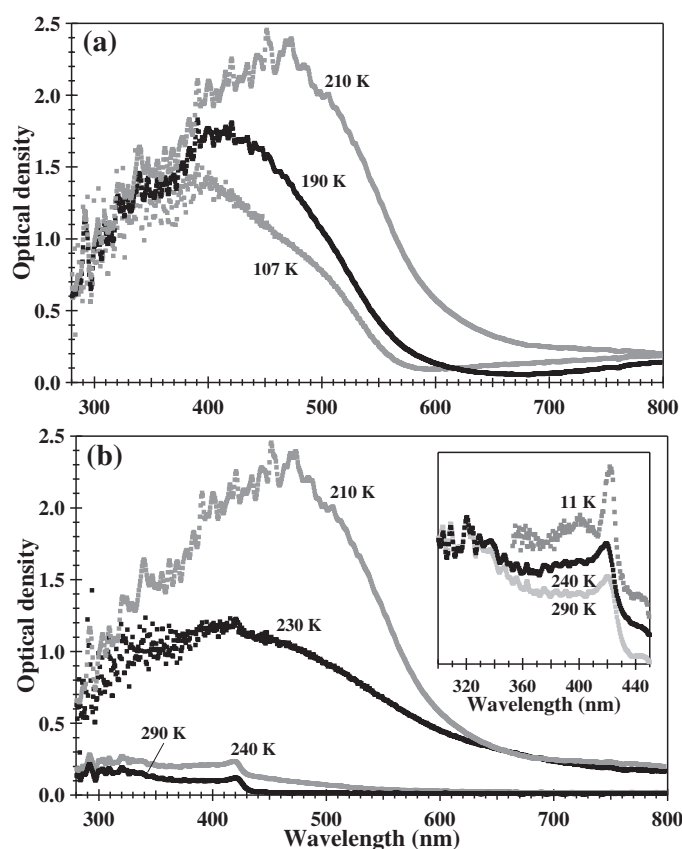
Figure 8. The temperature dependence of the optical density spectrum (curve 11 in figure 7) of iodine film on a sapphire substrate during heating: (a) $T \leqslant 210$ K, (b) $T \geqslant 210$ K. The exciton spectra at 240 and 290 K during heating are compared, together with the spectrum at 11 K, in the inset.

decrease. The tail may be due to excess iodine included tightly in AgI film. The absorptions between 370 and 410 nm correspond to the H_1 and H_2 exciton ones in polytype AgI (Mochizuki 2001), which are induced by some stacking disorder in the AgI lattice. This film was cooled again, down to 11 K, and the OD spectrum was measured. As indicated in the inset, a clear $Z_{1,2}$ absorption peak was observed at 422 nm, which indicates that the film is γ AgI, and this is discussed later in detail. Similarly to that for the iodine film evaporated at 96 K, the absorption increases with increasing temperature from 107 to 210 K. The band centred at about 470 nm, which appears as a shoulder at 107 K, becomes prominent. The spectral change may arise from the improvement in crystallinity of iodine domains upon heating (annealing). However, we cannot exclude effects of some particles (for example, $Ag_m I_n$) grown at the AgI/iodine interfaces. Therefore, we deposited iodine on a higher temperature substrate ($T_s > 96$ K) and measured the spectrum during deposition, as follows.

Figure 9 shows the time evolution of the OD spectrum of the film deposited on a sapphire substrate at 200 K during vacuum evaporation. Each measurement was made for 1400 ms at intervals of 3990 ms. The colour of the film was light brown. At the initial stage of the deposition, the spectrum consists of a broad band centred at 370 nm and a short wavelength absorption which increases toward some wavelength shorter than 330 nm. In the inset,
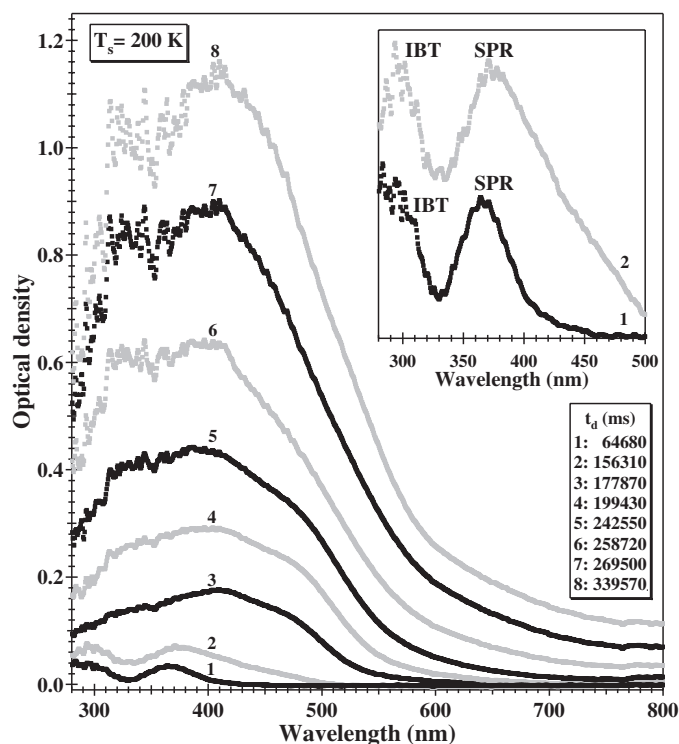
Figure 9. The time evolution of the optical density spectrum of the film on a sapphire substrate ($T_s = 200$ K) during deposition. Curves 1 and 2 are compared in the inset. SPR and IBT denote the surface plasmon absorption band and the interband transition band of silver particles deposited, Ag_n, respectively.

curves 1 and 2 are expanded and shown. These curves are very similar to those observed for silver clusters and microcrystals (Mochizuki and Ruppin 1993). The 370 nm band and short wavelength absorption are assigned to the collective mode resonance of valence electrons (so-called surface plasmon resonance (SPR)) and interband transitions (IBT) of silver particles (Ag_n: $n > 2$), respectively. Such absorptions indicate that silver atoms are also one of the vapour species for vacuum evaporation of AgI powder. At later times of deposition, the SPR band has a long wavelength tail, as shown in the inset. The tail is due to interaction between adjacent Ag_n, which was observed frequently in the spectra of gas evaporated Ag_n films (Hayashi *et al* 1990) and free Ag_n (Mochizuki and Ruppin 1993). Thus, it has been deduced spectroscopically that Ag atoms coming from the evaporation source condense to form Ag_n island film on the 200 K substrate at the initial stage of the deposition. In curve 6, at the middle stage of the deposition, a kink appears at about 415 nm. As discussed later, the kink is connected to the W_1 and W_2 exciton bands of AgI. The appearance of such an AgI-related kink means that vapour species diffuse easily and grow to become AgI particles in the iodine film matrix at 200 K. At the final stage of the deposition, the absorptions at wavelengths longer than 650 nm become prominent, forming the absorption edge structure of solid iodine. We cooled the specimen to 99 K and then elevated the specimen temperature to room temperature. We measured the spectra at different temperatures during the cooling and heating processes. The results are shown in figure 10. With cooling from 213 K, the absorption continues to increase and the maximum at about 420 nm shifts to about 430 nm at 99 K. With temperature increasing from 99 K, the absorption decreases monotonically. When the temperature exceeded 220 K,
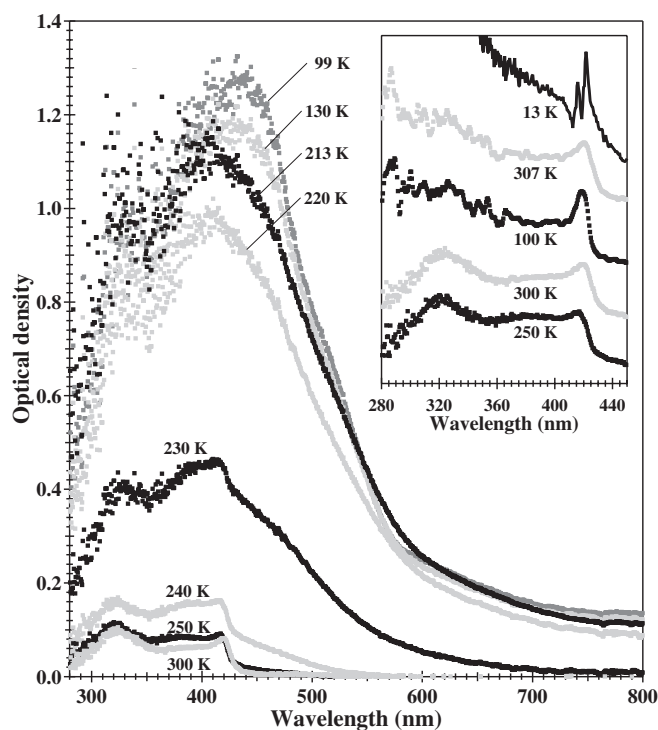
Figure 10. The temperature dependence of the optical density spectrum (curve 8 in figure 9) of the film on a sapphire substrate during cooling and heating processes. The exciton spectra during the cooling and heating processes are compared, together with the spectrum at 13 K, in the inset.

there was a faint exhaust sound from the vacuum pump attached to the specimen chamber, as heard for pristine iodine films. Simultaneously, the intense broad spectrum became weakened and it disappeared suddenly at 240 K, a weak spectrum peculiar to AgI emerging. Through different experiments, it was found that the spectral change temperature tends to vary with heating rate and film thickness. With temperature increasing from 240 to 300 K, the tail at wavelengths longer than 430 nm disappeared and the absorptions between 370 and 410 nm decreased. The tail may be due to some excess iodine included tightly in AgI films. The absorptions between 370 and 410 nm correspond to the H_1 and H_2 exciton ones in polytype AgI, which are induced by some stacking disorder in the AgI lattice. This film was cooled again, down to 13 K, and the OD spectrum was measured. The W_1, W_2 and W_3 exciton absorption bands are observed at 420, 414 and 320 nm, respectively. This indicates that the film is βAgI. In the inset, the spectra measured at 250 and 300 K for the first heating process, 100 K for the second cooling process and 307 K for the second heating process and 13 K for the third cooling process are compared. A remarkable change occurs at wavelengths shorter than 320 nm. A possible explanation for such spectral change is desorption of iodine from the film or reaction of imperfect AgI film with iodine during the heating and cooling processes.

3.4. Time evolution of the optical density spectrum of film deposited on a room temperature substrate during vacuum evaporation of AgI

We measured the time evolution of the OD spectrum of the film deposited on a room temperature sapphire substrate during vacuum evaporation. The evaporation condition is the same as in the experiments with the low temperature substrate. In order to study the optical spectrum for a
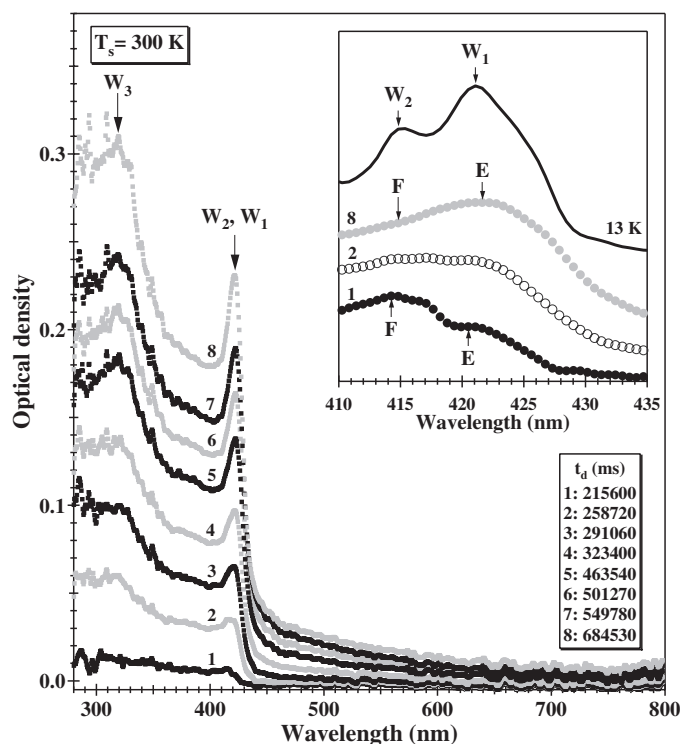
Figure 11. The time evolution of the optical density spectrum of the film on a sapphire substrate ($T_s = 300$ K) during deposition. The spectra at the initial and final stages of the deposition are compared, together with the spectrum at 13 K, in the inset.

wide thickness range, we performed successively the same depositions on the substrate. The results of the two successive deposition experiments are shown in figure 11. Each measurement was made for 1400 ms at intervals of 3990 ms. In the inset, the exciton spectra (curves 1, 2 and 8) at different stages of the deposition are compared after appropriate rescaling, together with the spectrum measured at 13 K. At the initial stage of deposition, two bands, E and F, appear at 420 and 414 nm, respectively. With progressing deposition, the absorption intensity of the E band becomes superior to that of the F band, and the J band at 320 nm becomes prominent. At the final stage of the deposition, the F band is merged with the E band, while the bands become well resolved at 13 K. At the initial stage of deposition, vapour species may condense on the substrate to form AgI microcrystal film. In the previous paper (Mochizuki and Umezawa 1997), we reported for AgI microcrystals that the $Z_{1,2}$ exciton band split into two bands centred at 420 nm and 415 nm due to the quantum size effects on the doubly degenerate valence band Γ_8 or some crystal field change at the crystallite surfaces due to surface reconstruction or surface defects or the appearance of the wurtzite modification. Since the intensity peak wavelengths of these bands are almost unchanged with progressive deposition, the E, F and J bands are assigned to the W_1, W_2 and W_3 exciton bands of βAgI (Cardona 1963, Mochizuki 2001, Mochizuki and Ohta 2000). Thus, the film deposited on room temperature sapphire substrate is optically identified with wurtzite phase AgI. The relative absorption increase of the W_1 (E) band with increasing deposition time (film thickness) may arise from the decreased exciton confinement and decreased surface (surface reconstruction and defects) effects. After the evaporation experiments, we measured the OD spectrum as a function of ageing time at 301 K.
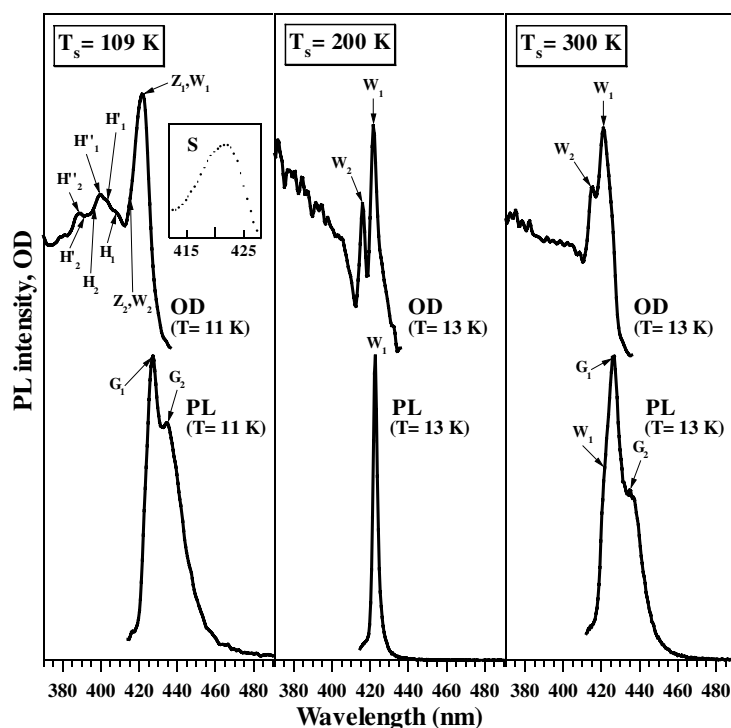
Figure 12. The optical density and photoluminescence spectra of different AgI films near 12 K.

It was found that the absorption at wavelengths shorter than 300 nm grows with increasing ageing time and, after 60 min, the spectrum comes to resemble that of pristine AgI (Cardona 1963, Mochizuki 2001, Mochizuki and Ohta 2000). This result is very similar to the result for the low temperature (200 K) substrate.

3.5. Photoluminescence of AgI films deposited on different temperatures of substrates

Figure 12 shows the OD and PL spectra of the AgI films deposited on the sapphire substrate at three different temperatures (109, 200 and 300 K). First, we discuss the spectra of the film deposited on the 200 K substrate. This film displays sharp well resolved absorption bands at 422 and 416 nm due to W_1 and W_2 excitons, respectively. The PL spectrum shows at 423 nm a sharp emission which has a full width at half-maximum (FWHM) of 79 cm^{-1} (approximately 10 meV) and with a very small Stokes shift (<7 meV) from the W_1 exciton absorption peak. Since the 7 meV shift is within the maximum systematic error between OD and PL measurements, the emission can be assigned to the radiative decay of free W_1 excitons.

The film deposited on the 109 K substrate shows an intense absorption band at 422 nm which coincides with the $Z_{1,2}$ and W_1 exciton wavelengths. However, this band is accompanied by a faint shoulder band (S) on the short wavelength side, as indicated by an arrow in the inset. The shoulder wavelength is close to that of the W_2 exciton. The 422 nm band and the shoulder may be assigned to the Z_1 and Z_2 exciton bands which are split by some crystal field change due to appearance of the wurtzite modification, or to defected βAgI. Incidentally, most of the $Z_{1,2}$ exciton absorption bands previously reported by different authors are also accompanied by a faint shoulder band at about 415 nm. It is also noted that a structured broad absorption band is seen between 380 and 415 nm, which had not been observed for other films. Similar absorption bands was observed previously at 405 and 398 nm for the film specimens (Mochizuki 2001),

which were assigned to the H_1 and H_2 excitons trapped at some stacking-disorder-induced polytype structures of βAgI. The 404 and 392 nm shoulders which are labelled respectively as H_1' and H_2', and the 400 and 389 nm peaks which are designated respectively as H_1'' and H_2'' are the exciton absorptions due to other types of polytype structure of βAgI. The PL spectrum of this film displays at least two broader bands. The intensity peaks at 434 and 427 nm which are designated respectively as G_2 and G_1 are observed, while the emission due to the radiative decay of free W_1 excitons is not clearly resolved. By comparing the PL spectral structure with the OD one, the G_1 and G_2 emissions are assigned to the radiative decays of excitons trapped at crystal defects.

The film deposited on the 300 K substrate shows also the W_1 and W_2 absorption bands which have larger FWHM than those of the film deposited on the 200 K substrate. This indicates the degradation of the crystallinity of βAgI. The G_1 and G_2 emissions are also observed. An extremely faint shoulder is observed at 422 nm. As for the film deposited on the 109 K substrate, the G_1 and G_2 emissions are due to the radiative decays of excitons trapped at crystal defects.

The above optical studies suggest that an optimum substrate temperature for fabricating βAgI film is close to 200 K.

3.6. Film formation by thermal evaporation of AgI powder in vacuum

The present studies have indicated optically that the species in the vapour zones produced by thermal evaporation of AgI powder are Ag atoms (Ag_1), silver iodide clusters (Ag_mI_n) and diatomic iodine molecules (I_2). As defined above, Ag_mI_n is the general term for AgI diatomic molecules, AgI clusters (($AgI)_n$) and nonstoichiometric silver iodide clusters (($AgI)_nAg_\delta$ ($\delta > 1$) and $(AgI)_nI_\varepsilon$ ($\varepsilon > 1$)). By the optical and time-of-flight mass spectroscopic methods, Bernstein (2003) has been studying Ag_mX_n (X: Cl, Br, I) particles (clusters) in an effort to understand the structure, dynamics and photochemistry of small clusters, and to explore the properties of larger Ag_mX_n structures as they grow from nanoclusters to the bulk material. We discuss the AgI film formation on the substrate whose temperature is below room temperature. We first note that iodine solid has the highest vapour pressure and I_2 molecules sublimate from the deposited film on a sapphire substrate prominently above 220 K under evacuation, as described above. The vapour species coming from the evaporation source arrive at the substrate surface and, when T_s is low enough to suppress re-evaporation, they are well adsorbed to form a composite film of Ag_1, Ag_mI_n and I_2. Since the rate of evaporation of I_2 is very high, Ag_1 and Ag_mI_n are thought be dispersed homogeneously in an iodine film matrix. These Ag_1 and small Ag_mI_n structures act as condensation nuclei for growing Ag_mI_n in the iodine film at later times. Incidentally, it is known that the cores of photographic sensitization AgI nuclei contain excessive iodine, producing the Ag_mI_n clusters. The composite film may display therefore a slightly different OD spectrum from that of pristine iodine film, as seen already in figures 1 and 7. When T_s is moderate, perhaps approximately 200 K, some of the adsorbed excess I_2 desorbs from the substrate, while Ag_1 and Ag_mI_n grow, generating larger Ag_n structures and larger Ag_mI_n structure, respectively, through some coalescence, absorption and reaction processes. Since the composite film, however, exhibited only the SPR absorption of Ag_n at the initial stage of the deposition, as shown in figure 9, the number of Ag_mI_n structures may be small in the film or the Ag_mI_n structures may be too small to display measurable optical absorption. With progressing deposition, the Ag_n acts as condensation nuclei, absorbing I_2 and small Ag_mI_n structures coming later from the evaporation source, generating larger nearly stoichiometric AgI particles. As a result, the kink at the exciton wavelength may appear in the OD spectrum of the composite film, as shown by curves 6, 7 and 8 in figure 9. Since I_2 neighbouring Ag_mI_n is thought to be bound more tightly in the composite film than in pristine iodine film,

different temperature dependences may be observed in the OD spectra of the pristine iodine and composite films, as shown in figures 4 and 10. Incidentally, the spectral structure is also affected, as shown in figures 3 and 9. When T_s is room temperature, re-evaporation of I_2 from the substrate, reactions and coalescence between adsorbed vapour species are enhanced, generating nearly stoichiometric AgI film, as shown in figure 11. The reactions, coalescences and annealing effects become promoted with T_s, while the re-evaporation and desorption of I_2 with increasing T_s are also promoted, increasing the deviation from the stoichiometric composition of AgI. Therefore, an optimum T_s for fabricating the highest quality AgI film below room temperature may exist. Since the film deposited on the 200 K sapphire substrate showed the sharpest OD and PL spectra, 200 K is thought to be the optimum T_s.

In the present discussion, we have ignored the effects of the kinds of substrate materials and the crystal orientation of the substrate surface. Up to the present, we have found the following substrate effects. When AgI powder is flash evaporated and deposited on different kinds of room temperature substrates (silica glass, sapphire single crystal and GaAs single crystal), β AgI tends to crystallize on the sapphire single-crystal and GaAs single-crystal substrates, while γ AgI tends to crystallize on the silica glass. Thus, there is a need to study the substrate effects. More detailed study with different kinds of substrate materials and with different orientations of substrate surfaces is in progress, in an attempt to fully explain the mechanism of AgI film formation.

4. Conclusion

We have evaporated AgI powder in vacuum by setting different evaporation conditions for the evaporation and deposition. The OD spectrum of AgI film on a substrate was measured as a function of the time elapsed from the beginning of the deposition for the first time. The same experiment was carried out for pristine iodine. Besides these vacuum evaporation experiments, we have produced two vertically well separated vapour zones of AgI above the evaporation source in a confined He gas atmosphere and obtained the optical extinction spectra as a function of the time elapsed after the beginning of evaporation. On the basis of these results, we have studied the process of AgI film formation on the low temperature (<room temperature) substrate and the following have been found.

(1) The vapour species produced by thermal evaporation of AgI powder in vacuum are Ag_1, $Ag_m I_n$ and I_2.
(2) The film deposited at low temperatures ($\leqslant$200 K) is a composite film. That is, Ag_1, Ag_n and $Ag_m I_n$ are dispersed in an iodine film matrix to form a composite film.
(3) Intense iodine optical absorption, which is slightly affected by Ag_1 and $Ag_m I_n$, has led many researchers to the wrong conclusion that amorphous AgI films prepared by quench deposition display strongly enhanced optical absorption in comparison to crystalline film.
(4) AgI film is grown through desorption of excess I_2 from the composite film and a coalescent reaction among film elements (Ag_1, Ag_n, $Ag_m I_n$ and I_2) with increasing temperature.
(5) The composite film grown on the substrate at 200 K becomes transformed to the spectroscopically best β AgI film by heating up to room temperature in vacuum.

The main limit of the present experimental technique is that there is no *in situ* characterization of the film thickness and crystal structure. Bearing these limits in mind, we have presented a reasonable connection between measured optical data and the AgI film formation process, with a convincing coherence with the results on pristine iodine, the vapour zone produced by thermal evaporation of AgI powder in a helium gas atmosphere confined at different pressures and the results obtained by the mass resolved excitation spectroscopy of an expansion cooled AgI beam.

Finally, a comparative study of the OD and PL spectra has also been performed at low temperature for the films deposited at different substrate temperatures. The exciton absorption band at 422 nm, which is usually assigned to $Z_{1,2}$ exciton absorption, has a faint short wavelength shoulder. The absorption intensity of the shoulder is dependent on the specimen preparation and the thermal history. The appearance of the shoulder has been explained by splitting of the doubly degenerate Γ_8 valence band. Such splitting may arise from some stress, with different thermal expansion coefficients for AgI and substrate materials (Mochizuki 2001), or some crystal field change due to mixing of the wurtzite (β) modification and stacking disorder due to nonstoichiometry. This speculation is in agreement with the well known result that γ AgI appears at room temperature as a metastable state and the stability of the γ phase is affected by slight nonstoichiometries and defects. Both the AgI films displaying the less resolved W_2 exciton absorption band and the $Z_{1,2}$ exciton absorption band with the short wavelength shoulder show a broader PL band and the long wavelength PL band. On the other hand, the AgI film displaying well resolved W_1 and W_2 absorption bands shows the sharpest single PL band. Therefore, the PL spectrum measurement could be a useful tool for characterizing the local structure in AgI film. On the basis of this notion, we are now developing nanometre-scale space resolved PL measurement with near-field optical microscopy.

Acknowledgments

References

Bernstein E R 2003 http://franklin.chm.colostate.edu/erb/home_metal.htm
Braner A A and Chen R 1963 *J. Phys. Chem. Solids* **24** 135
Burley G 1963 *Am. Mineral.* **48** 1266
Cardona M 1963 *Phys. Rev.* **129** 69
Dulin M N 1993 *Z. Phys.* D **26** 172
Fujishiro F and Mochizuki S 2002 *Nonlinear Opt.* **29** 443
Grimminger V H and Richter H 1956 *Z. Naturf.* a **11** 942
Hayashi S, Koga R, Ohtuji M, Yamamoto K and Fujii M 1990 *Solid State Commun.* **76** 1067
Kondo S, Itoh T and Saito T 1998 *Phys. Rev.* B **57** 13235
Many A, Simhony M, Weisz S Z and Levinson J 1961 *J. Phys. Chem. Solids* **22** 285
Mathieson L and Rees A L G 1956 *J. Chem. Phys.* **25** 753
Metropolis N 1939 *Phys. Rev.* **55** 636
Mochizuki S 1996 *J. Lumin.* **70** 60
Mochizuki S 2001 *Physica* B **308–310** 1042
Mochizuki S and Fujishiro F 2003a *J. Phys.: Condens. Matter* **15** 5057
Mochizuki S and Fujishiro F 2003b *Phys. Status Solidi* c **0** 763
Mochizuki S and Fujishiro F 2003c *Phys. Status Solidi* c **0** 767
Mochizuki S and Ohta Y 2000 *J. Lumin.* **87–89** 299
Mochizuki S and Ruppin R 1993 *J. Phys.: Condens. Matter* **5** 135
Mochizuki S and Umezawa K 1997 *Phys. Lett.* A **228** 111
Moss T S 1952 *Photoconductivity of the Elements* (London: Butterworths)
Satoko T 2003 private communication
Schnepp O, Rosenberg J L and Gouterman M 1965 *J. Chem. Phys.* **43** 2767
Stueber G J, Foltin M and Bernstein E R 1998 *J. Chem. Phys.* **109** 9831
Riggleman B M and Drickamer H G 1963 *J. Chem. Phys.* **38** 2721
Yamamoto H, Seki K, Mori T and Inokuchi H 1987 *J. Chem. Phys.* **86** 1775