JOURNAL OF
Materials
CHEMISTRY

Chemical bath deposition of {111} textured mercury(II) selenide thin layers on transparent polyester sheets

Biljana B. Pejova,[*a] **Metodija Ž. Najdoski,**[a] **Ivan S. Grozdanov**[a] **and Sandwip K. Dey**[b]

[a]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, POB 162, Arhimedova 5, 91000 Skopje, Republic of Macedonia. E-mail: biljana@iunona.pmf.ukim.edu.mk*
[b]*Department of Chemical, Bio, and Materials Engineering, Arizona State University, Tempe, Arizona 85287-6006, USA*

Received 7th July 1999, Accepted 24th August 1999

A novel method for mercury(II) selenide thin film deposition on transparent polyester sheets is presented. The method is based on chemical bath deposition in alkaline media, the chemical reaction involved being hydrolytic decomposition of selenosulfate. X-Ray analysis confirmed that the deposited material is {111} textured mercury(II) selenide. The sheet resistances of the annealed films are about 1.32 kΩ cm^{-2} and for as-deposited samples are about 10 times higher. The absorption onset is strongly blue-shifted from the bulk value. This is attributed to size quantization in the *ca.* 8 nm nanocrystals.

1 Introduction

There has been an increased interest in depositing electroconductive films on non-conductive organic polymers in the last few years.[1–10] This is due to the possibility for their application in various fields of optoelectronic technology, such as fabrication of display devices,[11] optoelectronic devices,[12] as well as active electrode materials in energy storage.[13]

Several techniques for the preparation of HgSe thin solid films on various substrates have been reported so far. Becker *et al.* reported a molecular beam epitaxial growth method for the preparation of HgSe thin films on GaAs substrates.[14] The same technique has been applied by Einfeldt *et al.*, who used ZnSe substrates and investigated the electrical properties of the HgSe–ZnSe heterojunctions.[15] The latest system may be used for blue/green laser diode and light emitting diode fabrication, which have been investigated thoroughly by Yu *et al.*[16] Pramanic *et al.* have reported an aqueous reactive solution growth technique[17] for HgSe thin film deposition on glass substrates, starting from mercury(II) formamide and sodium selenosulfate as a selenide-releasing agent. The films obtained by their method are amorphous and p-type semiconductors.

This paper presents a novel method for chemical bath deposition of HgSe thin films on non-conductive polyester substrates. The proposed method is very simple, non-hazardous and allows relatively fast deposition of HgSe films, from one chemical bath, under moderate experimental conditions. Common and inexpensive chemicals are used for the fabrication of the films and the proposed technique is convenient for both small- and large-area deposition. The basic morphological, optical and electrical characteristics of the films are also reported. The mechanical properties of the substrate used allow various possible applications for the obtained thin films.

2 Experimental

The suggested method is very simple and the deposition can be performed in beakers or plastic vessels. Any shape or size of substrate can be used.

2.1 Preparation of the substrates

Thin solid films of mercury(II) selenide were prepared on transparent uncoated polyester substrates, such as the transparent films commonly used for overhead projectors (ZweckForm, catalogue no. 3555). Substrate sizes were the same as those of a standard microscope glass. Before deposition, substrates were cleaned in a warm detergent solution for 15 min. Then they were rinsed with deionized water and immersed in a fresh 0.03% aqueous solution of tin(II) chloride for 15 min. The treatment with tin(II) chloride solution provides a uniform wetting of the substrate surface and improves the film adhesion.

2.2 Deposition of the HgSe films

The technique for chemical bath deposition of HgSe was similar to that which we used earlier to deposit thin Cu_2Se films.[18] Previously prepared substrates were vertically supported against the walls of a 100 cm^3 laboratory beaker which contained the solution for chemical deposition. This solution was prepared by mixing 10 cm^3 of a 0.15 mol dm^{-3} aqueous solution of $Hg(NO_3)_2$ with 4 cm^3 25% $NH_3(aq)$, cooling this system to 10 °C and adding 20 cm^3 of previously cooled Na_2SeSO_3 solution. This was prepared in the following manner: 8 g selenium was mixed with a small portion of 1 mol dm^{-3} aqueous solution of sodium sulfite and, when a dense suspension was obtained, the remainder of the 100 cm^3 of sodium sulfite solution was added. The obtained system was then heated at 90 °C for about one hour. After cooling to room temperature, the suspension was filtered off and deionized water was added to the filtrate to bring the total volume of the solution up to 100 cm^3.

The temperature was kept constant at 10 °C during deposition. The dependence of film thickness on deposition time is shown in Fig. 1. As can be seen, the deposition is practically complete after about 3 h. The final thickness of the films is about 270 nm. Thicker films can be prepared by re-inserting the initially deposited HgSe films into a fresh bath.

2.3 Physical measurements of the films

The sheet resistance of the films was measured between two silver-pasted electrodes, 1 cm in length and 1 cm apart, using a

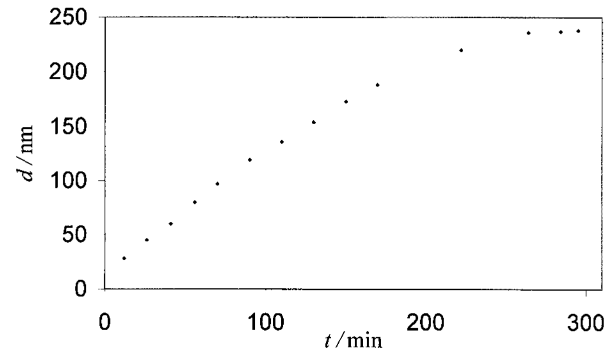

Fig. 1 The dependence of film thickness on deposition time.

Radio Shack Digital Multimeter model 22-168. The thickness of the films was determined by the gravimetric method. The deposited films, as well as the bulk precipitates, were studied by X-ray diffraction, using a Rigaku model D/MAX-IIB diffractometer and nickel-filtered Cu-Kα radiation. The optical spectra were recorded on a Cary 5 spectrophotometer in the VIS–NIR spectral region.

3 Results and discussion

3.1 Chemical considerations

The overall chemical reaction of the deposition process may be represented with the following equation:

$$Hg^{2+} + SeSO_3^{2-} + 2OH^- \rightarrow HgSe + SO_4^{2-} + H_2O \quad (1)$$

First, a white precipitate is formed as a result of the reaction between mercury(II) nitrate and ammonia:

$$Hg^{2+} + NO_3^- + 2NH_3 \rightarrow [HgNH_2]NO_3 + NH_4^+ \quad (2)$$

The excess ammonia reacts partly with the precipitate, forming a variety of complexes (with 1, 2, 3 and 4 ligand molecules):

$$[HgNH_2]NO_3 + (x-1)NH_3 + H_2O \rightarrow [Hg(NH_3)_x]^{2+} + NO_3^- + OH^- \text{ where } x \in \{1,2,3,4\} \quad (3)$$

The rest of the precipitate dissolves with the addition of selenosulfate solution:

$$[HgNH_2]NO_3 + xSeSO_3^{2-} + H_2O \rightarrow [Hg(SeSO_3)_x]^{(2x-2)-} + NO_3^- + NH_3 + OH^- \quad (4)$$

With the excess sodium sulfite which did not react with selenium, formation of other complexes is possible, also causing dissolution of the precipitate:

$$[HgNH_2]NO_3 + xSO_3^{2-} + H_2O \rightarrow [Hg(SO_3)_x]^{(2x-2)-} + NO_3^- + NH_3 + OH^- \quad (5)$$

Of course, the possible formation of mixed complexes such as $[Hg(NH_3)_x(SeSO_3)_y(SO_3)_z]^{(2y+2z-2)-}$ (where $x+y+z \leqslant 4$) cannot be excluded. Thus the complexity of this system is obvious. However, the free mercury(II) ions (although present in rather small concentrations) react with the selenide ions released by the following reaction:

$$SeSO_3^{2-} + H_2O \rightarrow Se^{2-} + SO_4^{2-} + 2H^+ \quad (6)$$

finally forming HgSe films:

$$Hg^{2+} + Se^{2-} \rightarrow HgSe \quad (7)$$

The concentration of free mercury(II) ions may be considered practically constant during deposition, since it is controlled by the dynamic equilibrium between precipitation and dissociation of the complexes.

During the largest part of the deposition process, bulk precipitation is observable, accompanied by scattering of coherent laser light. At the end of the deposition, the bulk precipitation reduces and, therefore, so does the scattering. Thus it can be concluded that the predominant deposition mechanism is the cluster one (although not to the exclusion of the ion-by-ion route, at least at the end of the deposition process), where the clusters are probably colloids of a Hg amido species, such as that in eqn. (2).

A thorough study of the deposition mechanism for CdSe thin layers has been recently reported, with an emphasis on the quantum size effects.[19]

3.2 X-Ray investigations

X-Ray diffractograms (produced with nickel-filtered Cu-Kα radiation) of both as-deposited and annealed (120 °C for 5 h) HgSe thin films are shown in Fig. 2(a) and (b), respectively. As is obvious, one highly intense peak appears at θ 12.677°. X-Ray diffractograms were also recorded from the bath precipitate [Fig. 2(c)]. Comparison of the observed diffraction peaks with the standards (JCPDS powder diffraction data set no. 15-456 from the 1-46 database) confirmed that most of the deposited material is the cubic form of mercury(II) selenide (known as tiemannite). The Miller indices in the diffractograms were taken from the previously mentioned database. As can be seen from the X-ray diffractograms, the HgSe thin films show strong {111} texturing. It has been already shown that all synthetic mercury selenides show the sphalerite type structure.[20] On the basis of the full width at half maximum of the XRD peaks, using the Debye–Scherrer expression[21,22] we have calculated the average crystal sizes of the unannealed and annealed films. The corresponding values are 7.7 and 7.9 nm. The slight increase in crystal size upon annealing is reflected in the appearance of the optical spectra of the films (exhibiting a slight red-shift—see below). A dark-field microphotograph of a thin film with a thickness of 2.23 μm is shown in Fig. 3. As can be seen from the microphotograph, the obtained films are characterized by a uniform and homogeneous microstructure.

3.3 Optical investigations

Optical absorption spectra in the UV–VIS–NIR region were recorded for the obtained mercury(II) selenide thin films. The spectra for two films (taken against a substrate reference), with thicknesses of 28 and 59 nm, as well as for the substrate (taken against the air reference), are shown in Fig. 4. As is obvious, the obtained thin films are practically transparent in the 800–2000 nm region. Using the optical absorption data, the optical

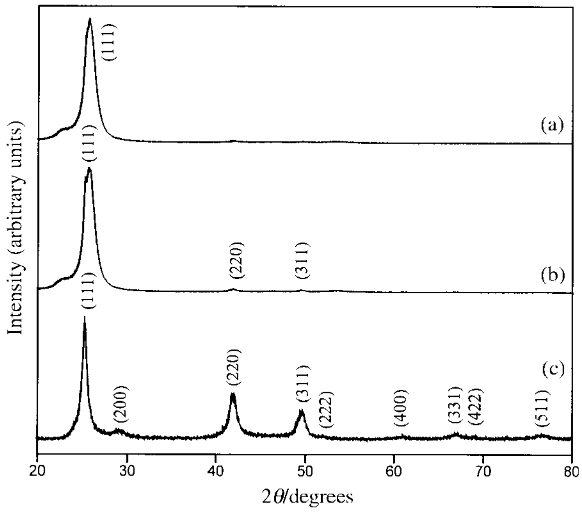

Fig. 2 X-Ray diffractograms of: (a) as-deposited films; (b) annealed films; (c) bulk precipitate.

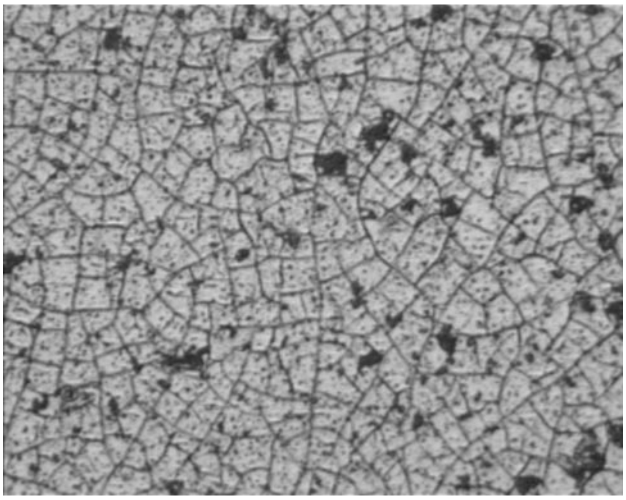

Fig. 3 Dark-field microphotograph of a thin film with a thickness of 2.23 μm.

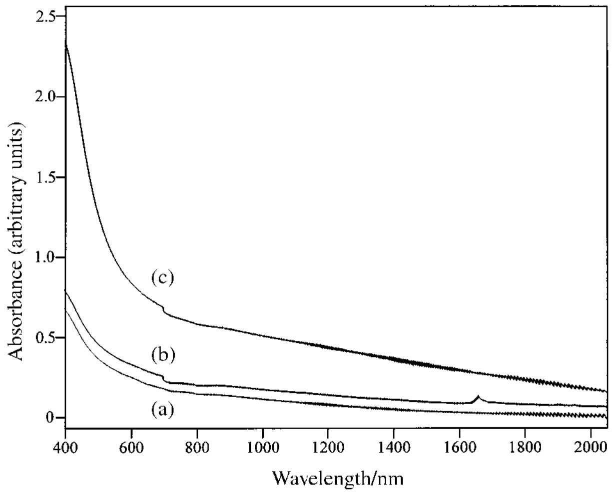

Fig. 4 Optical spectra of: (a) polymer substrate; (b) film with a thickness of 28 nm; (c) film with a thickness of 59 nm.

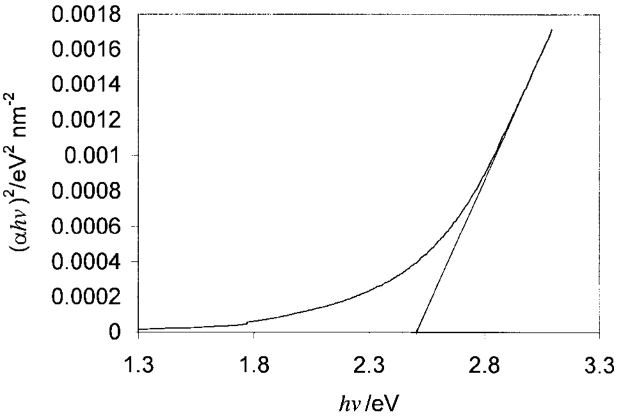

Fig. 5 A plot of $(\alpha h\nu)^2$ *vs.* E.

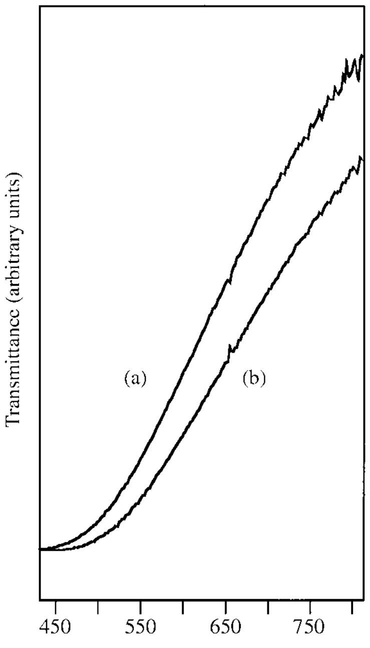

Fig. 6 Optical spectra of the as-deposited film (a) and the annealed film (b), exhibiting a red-shift.

bandgap of the HgSe films was determined from a plot of $(\alpha h\nu)^2$ *vs.* E (Fig. 5). It is well known that for direct transitions $(\alpha h\nu)^{1/n}$ depends linearly on the photon energy, where $n = 1/2$ or 3/2 depending on whether the transitions are allowed or forbidden. In the case of HgSe films, the best fit of $(\alpha h\nu)^{1/n}$ *vs.* the photon energy was obtained for $n = 1/2$. Extrapolation of the linear part gave a bandgap energy of 2.50 eV for the unannealed films, while for the annealed films it reduces to 2.44 eV. A value of 1.42 eV has been previously reported for amorphous HgSe films.[17] However, the conclusion regarding the amorphous character of the films reported in ref. 17 is based solely on the absence of sharp peaks in the X-ray diffractograms. On the other hand, novel investigations in the field of nanocrystalline materials have shown that materials with excellent crystallinity can show very broad peaks (sometimes even none) in their XRD spectra.[23] It is known that (bulk) HgSe has an inverted band structure (this means a negative value for the bandgap energy[24]). In fact, the rather large positive values for the bandgap measured both in ref. 17 and in our case may be attributed to size quantization effects.[19,25,26] Strong quantum size effects for colloidal HgSe have been thoroughly studied by Nedeljkovic *et al.*[27] They report a value of 3.15 eV for the bandgap in colloidal particles with an average size between 2 and 3 nm. Since the average size of these HgSe colloidal particles is smaller than the average crystal size in the case of our films, a higher bandgap energy is expected. The size quantization in the case of our films is also reflected in the appearance of the optical spectra. In Fig. 6, optical spectra (taken against the substrate reference) for both unannealed and annealed films are shown. As can be seen, a red-shift is clearly observable upon annealing, indicating an increase in the crystal size. The observed red-shift is in line with the decrease of the bandgap energy, due to size quantization effects.

3.4 Electrical investigations

The measured electric resistance values for the as deposited films are about 13 kΩ cm^{-2}. Upon annealing (in air), due to the crystallization process, the electrical resistance decreases by about ten times. In Fig. 7, the dependence of the sheet resistance (measured between two silver pasted electrodes 1 cm apart and 1 cm long) on temperature is presented (in a semi-logarithmic diagram). Between points A and B the sheet resistance slowly decreases, the predominant reason for this being the simple dependence of the electrical resistance on temperature. After point B, the decrease is much more pronounced. We suppose that a possible reason for this could be the beginning of the crystallization process at point B. The annealing time required to achieve a constant sheet resistance (which might imply ending of the crystallization) was determined from the dependence of this quantity on the annealing time. The results are presented in Fig. 8, from which

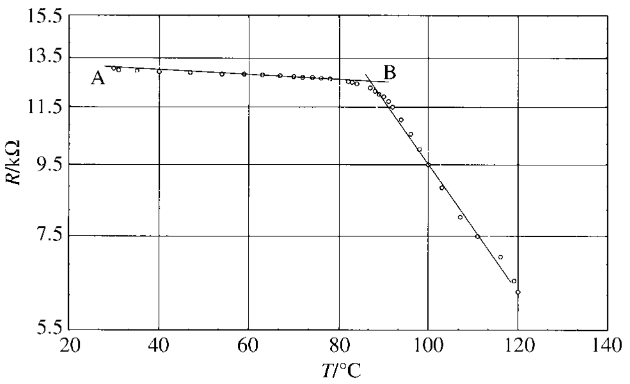

Fig. 7 The dependence of sheet resistance on temperature (semilogarithmic plot).

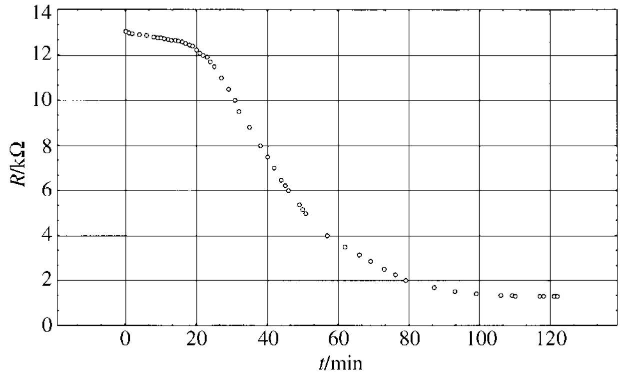

Fig. 8 The dependence of sheet resistance on annealing time.

it follows that after about 110 min no significant changes in the sheet resistance were observed. The observed changes of electrical resistance with temperature are irreversible, in line with the previous conclusions.

4 Conclusions

A simple bath deposition technique for HgSe film deposition on polyester substrates has been described. The technique is straightforward, economic and offers the possibility of large area depositions. The obtained HgSe films are crystalline, $\{111\}$ textured, uniform and specularly reflective. Upon annealing the average crystal size increases slightly, which is also evident from the optical spectra. Some basic optical and electrical observations for the as-deposited as well as for the annealed HgSe films have also been reported. The relatively high bandgap energy (2.50 eV for unannealed and 2.44 eV for the annealed films) may be attributed to size quantization effects. The sheet resistances of the annealed films are *ca.* 1.32 kΩ cm^{-2} and for as-deposited films are about 10 times higher.

Acknowledgements

This work was carried out under a Macedonian–US joint research project sponsored by the Governments of the Republic of Macedonia and the USA. The financial support of both governments is gratefully acknowledged. The X-ray data were obtained on equipment purchased under National Science Foundation, USA, grant no. DMR-8406823. The valuable contribution of Professor Gary Hodes to the final form of the paper is gratefully acknowledged.

References

1 M. Inouoe, C. Cruz-Vazquez, M. B. Inoue, K. W. Nebesny and Q. Fernando, *Synth. Met.*, 1993, **55**, 3748.
2 T. Yamamoto, K. Tanaka, E. Kubota and K. Osakada, *Chem. Mater.*, 1993, **5**, 1352.
3 D. C. Trivedi and S. K. Dhawan, *Synth. Met.*, 1993, **59**, 267.
4 N. Mori, *J. Appl. Phys.*, 1993, **73**, 1327.
5 J. V. Mantese, A. L. Micheli, A. B. Catalan and N. W. Schubring, *Appl. Phys. Lett.*, 1994, **64**, 3509.
6 L. T. Chang and C. C. Yen, *J. Appl. Polym. Sci.*, 1995, **55**, 371.
7 G. Appel, A. Yfantis, W. Gopel and D. Schmeisser, *Synth. Met.*, 1996, **83**, 197.
8 Y. Sun and E. Ruckenstein, *Synth. Met.*, 1996, **82**, 35.
9 M. A. B. Meador, D. Hardygreen, J. V. Auping, J. R. Gaier, L. A. Ferrara, D. S. Papadopoulos, J. W. Smith and D. J. Keller, *J. Appl. Polym. Sci.*, 1997, **63**, 821.
10 N. E. Belhadjtahar, O. Meyer and A. Fourrierlamer, *IEEE Trans. Microwave Theory Tech.*, 1997, **45**, 260.
11 S. K. Dhawan and D. C. Trivedi, *J. Appl. Electrochem.*, 1992, **22**, 563.
12 G. Gustaffson, Y. Cao, G. M. Treacy, F. Clavetter, M. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477.
13 C. Gasgrande, S. Ponero, P. Prosperi and B. Skrosati, *J. Appl. Electrochem.*, 1992, **22**, 195.
14 C. R. Becker, L. He, S. Einfeldt, S. Y. Wu, G. Lerondel, H. Heinke, S. Oehling, R. N. Bicknell-Tassius and G. Landwehr, *J. Cryst. Growth*, 1993, **127**, 331.
15 S. Einfeldt, H. Heinke, M. Behringer, C. R. Becker, E. Kurtz, D. Hommel and G. Landwehr, *J. Cryst. Growth*, 1994, **138**, 471.
16 Z. Yu, J. Ren, J. W. Cook and J. F. Schedzina, *Physica B* (*Amsterdam*), 1993, **119**, 119.
17 P. Pramanic and S. Bhattcharya, *Mater. Res. Bull.*, 1989, **24**, 945.
18 I. Grozdanov, *Synth. Met.*, 1994, **63**, 213.
19 S. Gorer and G. Hodes, *J. Phys. Chem.*, 1994, **98**, 5338.
20 N. Z. Boctor and G. Kullerud, *J. Solid State Chem.*, 1986, **62**, 177.
21 H. S. Peiser, H. P. Rooksby and A. J. C. Wilson, *X-Ray Diffraction by Polycrystalline Materials*, Chapman & Hall, London, 1960.
22 M. G. Bawendi, A. R. Kortan, M. L. Steigerwald and L. E. Brus, *J. Chem. Phys.*, 1989, **91**, 7282.
23 G. Hodes, personal communication.
24 Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik*, Springer-Verlag, Berlin, 1955.
25 Y. Mastai and G. Hodes, *J. Phys. Chem. B*, 1997, **101**, 2685.
26 Y. Wang and N. Herron, *J. Phys. Chem.*, 1991, **95**, 525.
27 J. M. Nedeljkovic, M. T. Nenadovic, O. I. Micic and A. J. Nozik, *J. Phys. Chem.*, 1986, **90**, 12.

Paper 9/05452I