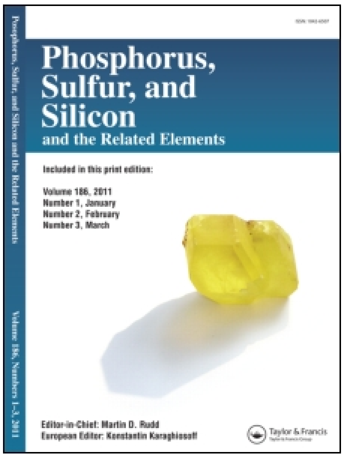

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CONTROL OF PEELING DURING CHEMICAL DEPOSITION OF THIN FILMS OF Bi_2S_3 BY SURFACE PRETREATMENT WITH FUNCTIONALIZED SILANES

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CONTROL OF PEELING DURING CHEMICAL DEPOSITION OF THIN FILMS OF Bi_2S_3 BY SURFACE PRETREATMENT WITH FUNCTIONALIZED SILANES

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Dedicated to Professor Reinhard Schmuzler on the occasion of his 60th birthday.

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Clean glass surfaces have been treated with a series of compounds having the general formula, $(CH_3O)_3Si(CH_2)_3X$, where X is a selected functional group. Thin films of Bi_2S_3 were then deposited on the treated surfaces. The tendencies of the films to peel were observed as X was varied. The greatest resistance to peeling occurred when X was SH or $(CH_2)_{14}CH_3$. Scanning electron microscopy showed that Bi_2S_3 films deposited on the surfaces having terminal SH groups had smaller particle size, were more homogeneous in appearance and possessed smaller intercrystalline voids than those deposited on untreated surfaces. The improvement of resistance to peeling after treatment with $(CH_3O)_3Si(CH_2)_3SH$ is explained in terms of the formation of an initial glass-O-Si bond and the subsequent formation of a covalent Bi-S bond to the silane layer bound to the glass. Although the films prepared with X as $(CH_2)_{14}CH_3$ did not peel readily, they were easily separated from the glass surface by mechanical means.

Key words: Thin films, silanes, electron microscopy, bismuth sulfide.

INTRODUCTION

Thin films of heavy metal chalcogenides have been used commercially and a number of future important uses seem possible. For example, since the early 1950's chemically deposited thin films of PbS and PbSe have found both military and civilian applications as detectors of infrared radiation. More recently, chemically deposited thin films of metal chalcogenides have been incorporated into solar cell structures.[1] Chemically deposited thin films of Bi_2S_3 have been shown to possess properties which make it a good candidate for solar energy applications.[2–7] Another interesting property which may find practical use is metal sulfide thin film photography.[8] In applications, the chemical deposition process offers a number of clear advantages. The method is inexpensive, it requires no costly sophisticated equipment and it is possible to coat very large surface areas as well as surfaces having virtually any geometric shape.

One problem often encountered in the chemical deposition process is that of peeling. Following a certain period of deposition time, the film being deposited separates from the glass surface. Factors which affect peeling include the manner of cleaning of the surface, the chemical composition of the bath, the duration of the deposition process and the time which elapses between removal of the film from the bath and drying. Methods which have been tried to inhibit peeling include "double dip" deposition,[3,9] which involves an initial costing carried out for a short period of time followed by immersion into a fresh coating bath for a substantially longer period. A method which has been successful in inhibiting peeling involves the deposition of an initial coating of zinc sulfide upon which is deposited a film of bismuth sulfide.[10]

In the present study we have investigated the pretreatment of glass surfaces with five reagents having the general formula $(H_3CO)_3Si(CH_2)_nX$, where X is a terminal functional group. Following such treatment, the surfaces were subsequently coated with Bi_2S_3. The effect of such treatments with respect to their ability to inhibit the peeling process have been noted and interpreted in terms of the chemical properties of X.

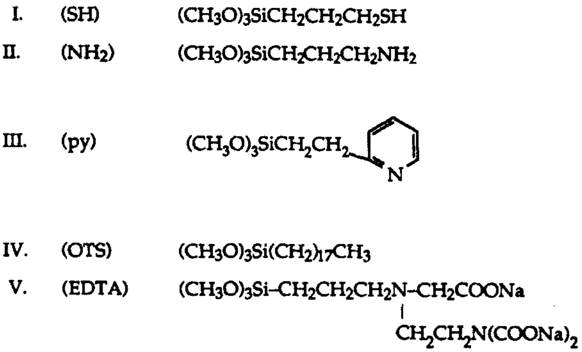
EXPERIMENTAL

Materials. Microslides, 1 × 3 inch, were purchased from the Corning Glass Company. Methanol and toluene, analytical grade, were purchased from EM Scientific. The organosilane compounds were purchased from Hüls America, Inc. and they are identified below (Scheme I).

Preparation of Substrates. Glass slides were cleaned with a solution of Cheer detergent by scrubbing with a soft cotton cloth, followed by repeated rinsing with deionized water and then with methanol. The cleaned slides were air-dried and used in subsequent experiments.

Preparation of SH-Surfaces.[11] In a plastic beaker, 1.5 ml of reagent I and 5 drops of glacial acetic acid were mixed with 150 ml toluene. After the solution was stirred at room temperature for 30 min, four slides were mounted vertically with respect to the wall of the beaker. The slides were removed at intervals of 2 min, 15 min, 30 min, and 45 min followed by a thorough rinsing with toluene and baked at 100° for an hour. These surfaces will be referred to as SH-surfaces.

Preparation of NH_2-Surfaces. The procedure described for SH-surfaces was used. The only changes made were (a) 1.5 ml of reagent II was substituted for reagent I, (b) a mixture of 135 ml of methanol and 15 ml of deionized water served as the solvent and (c) the slides were rinsed with methanol after silanization. These surfaces will be referred to as NH_2-surfaces.



I.	(SH)	$(CH_3O)_3SiCH_2CH_2CH_2SH$
II.	(NH_2)	$(CH_3O)_3SiCH_2CH_2CH_2NH_2$
III.	(py)	$(CH_3O)_3SiCH_2CH_2$
IV.	(OTS)	$(CH_3O)_3Si(CH_2)_{17}CH_3$
V.	(EDTA)	$(CH_3O)_3Si\text{-}CH_2CH_2CH_2N(CH_2CH_2N(COONa)_2)\text{-}CH_2COONa$

Scheme I The organosilanes used to modify the surface of glass substrate.

Preparation of py-Surfaces. The procedure just described for SH-surfaces was used. The only change made was that 1.5 ml of reagent III was substituted for reagent I. These surfaces will be referred to as py-surfaces.

Preparation of OTS-Surfaces. The procedure described for SH-surfaces was used except for the substitution of reagent I by reagent IV. These surfaces will be referred to as OTS-surfaces.

Preparation of EDTA-Surfaces. A solution was prepared from 1 ml of the trisodium salt of N-[3-trimethoxysilylpropyl]ethylenediaminetriacetic acid (reagent V, 50% aqueous solution as purchased), 15 ml of deionized water and 135 ml of methanol which was stirred and heated in a water bath at 60° for 30 min. After that period of time, four slides were immersed in the solution for 2 min, 15 min, 30 min, and 45 min. Following their removal they were rinsed thoroughly with methanol and baked at 110° for an hour. These surfaces will be referred to as EDTA-surfaces.

Deposition of Bi_2S_3 Films. The Bi_2S_3 films were deposited using a previously described procedure.[3] A solution of 0.5 M bismuth nitrate was prepared by dissolving 24.25 g of $Bi(NO_3)_3 5H_2O$ in 70 ml of triethanolamine/water solution (1:1 by volume) and then was taken to a volume of 100 ml with deionized water. The deposition bath was prepared using 10 ml of the bismuth solution, 8 ml of triethanolamine/water (1:1 by volume), 4 ml of 1 M thioacetamide, and 78 ml of deionized water.

The general procedure was as follows: during "single dip" deposition, groups of four untreated glass slides or slides which were treated in organosilane solutions for 15 min were mounted in 100 ml of a freshly prepared deposition bath supported by the wall of the beaker. The films were grown at room temperature for periods of 2 h, 3.5 h, 5 h, and 6.5 h, respectively, then rinsed and dried in air. In the "double dip" deposition method, groups of four slides first underwent a 4 hr deposition, and were then rinsed and dried in air. Except for those deposited on EDTA-surfaces, the films remained intact and uniform at this stage. They were transferred to a second bath and the deposition was allowed to proceed for an additional 2 to 6.5 hrs, then rinsed and dried in air.

All subsequent physical measurements on the bismuth sulfide thin films were performed on the side which faced the wall of a beaker. The thin films on the other side usually did not appear uniform because of the precipitate which settled gravitationally on the surface.

Measurements. X-ray photoelectron spectroscopy (XPS) multiplex measurements were carried out on a Perkin-Elmer PHI 5500 ESCA unit Mg-K_α X-ray. Scans of 200 sweeps were used for nitrogen and 20 sweeps were used in scanning for other elements including carbon, oxygen, and silicon. All samples used in XPS analysis were handled with gloves.

Advancing contact angle measurements were performed with a Rame-Hart goniometer under ambient conditions. Double distilled water was used in the measurement. Three or four drops were measured for each surface and the values averaged. An untreated glass surface used was cleaned with detergent, followed by a thorough rinsing, and then heated at 110° for an hour. The modified surfaces used were those that were treated in an organosilane solution for 15 min.

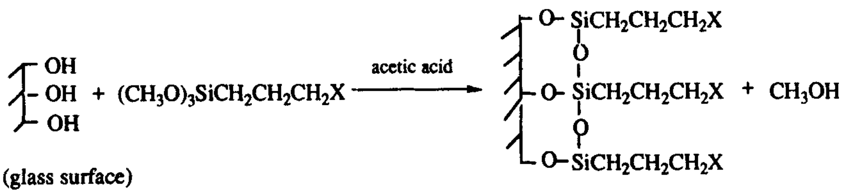
Scanning electron microscopy (SEM) was performed with Joel JSM 6400 (25 kV × 43,000 and 20 kV × 20,000). Bi_2S_3 thin films examined were deposited for 10, 30 and 240 minutes on an untreated glass surface or on an SH-surface prepared by a 15 min treatment with 3-mercaptopropyltrimethoxysilane.

Elemental analysis was provided by Galbraith Laboratories, Inc.: C, 21.24; S, 14.74; and Bi, 32.46 percent, respectively, for a sample of the powdered material prepared by the direct reaction of 3-mercaptopropyltrimethoxysilane with a solution of $Bi(NO_3)_3$.

RESULTS AND DISCUSSION

Silanization of Glass Surfaces

The organosilane reagents used in this study react with glass surfaces with the formation of covalent bonds between the organosilanes and the glass surface.[12,13] Condensation may also occur among silane molecules to form Si-O-Si cross-linkages when water is present as indicated in the following scheme. The thickness of the organosilane layer formed by self-assembled condensation may vary depending on the extent of cross-linking.



X = different functional groups

Scheme II The silanization at the surface of a glass substrate.

TABLE I

Chemical analyses on the surfaces of substrates by XPS

Surfaces	Silanization time (min)	Atomic composition (%)*
glass	0	N 0.0; S 0.0; Si 23.3; O 59.5; C17.2
SH-surface (from ref. 11)	2	S 2.3; Si 21.3; O 50.5; C 25.9
	15	S 2.9; Si 19.7; O 48.2; C 29.2
	30	S 3.2; Si 18.7; O 46.2; C 32.0
	45	S 4.7; Si 18.0; O 43.2; C 34.2
NH_2-surface (from ref. 11)	2	N 2.0; Si 21.3; O 48.4; C 28.3
	15	N 3.0; Si 20.8; O 46.8; C 29.3
	30	N 3.5; Si 20.5; O 44.9; C 31.0
	45	N 3.4; Si 19.9; O 46.0; C 30.6
py-surface	2	N 2.4; Si 20.8; O 52.5; C 24.3
	15	N 3.5; Si 18.8; O 49.1; C 28.6
	30	N 3.9; Si 19.5; O 46.4; C 30.2
	45	N 4.1; Si 19.1; O 44.7; C 32.1
EDTA-surface	2	N 2.1; Si 24.6; O 55.6; C 17.7
	15	N 3.0; Si 23.5; O 53.5; C 20.0
	30	N 3.4; Si 24.0; O 56.2; C 24.0
	45	N 3.8; Si 23.6; O 54.2; C 18.4

* The relative molar percents of the selected elements are listed. Trace amounts of sodium, calcium, and magnesium existing in glass are excluded and the numbers have been normalized to 100%. The errors in the values given are 0.1 to 0.15 of their magnitude.

The silanization of the glass substrate was monitored by XPS when the silane reagent contained an element different from Si, O or *adventitious carbon* present in the glass substrate. The analytical data for these surfaces are summarized in Table I.

The detailed XPS results for SH-surface and NH_2-surface[11] have been submitted elsewhere and will be described only briefly here. For the SH-surface, two peaks at 166.5 eV and 171.5 eV were observed and attributed to S2p, with the former arising from the thiol and the other possibly arising from oxidized sulfur species generated by reaction of the thiol with oxygen adsorbed on the surface; on the NH_2-surface the N1s peak was observed at 402.0 eV. On py-surfaces, a nitrogen peak N1s (402.1 eV) was detected after 2 minutes of treatment in a 2-trimethoxy-

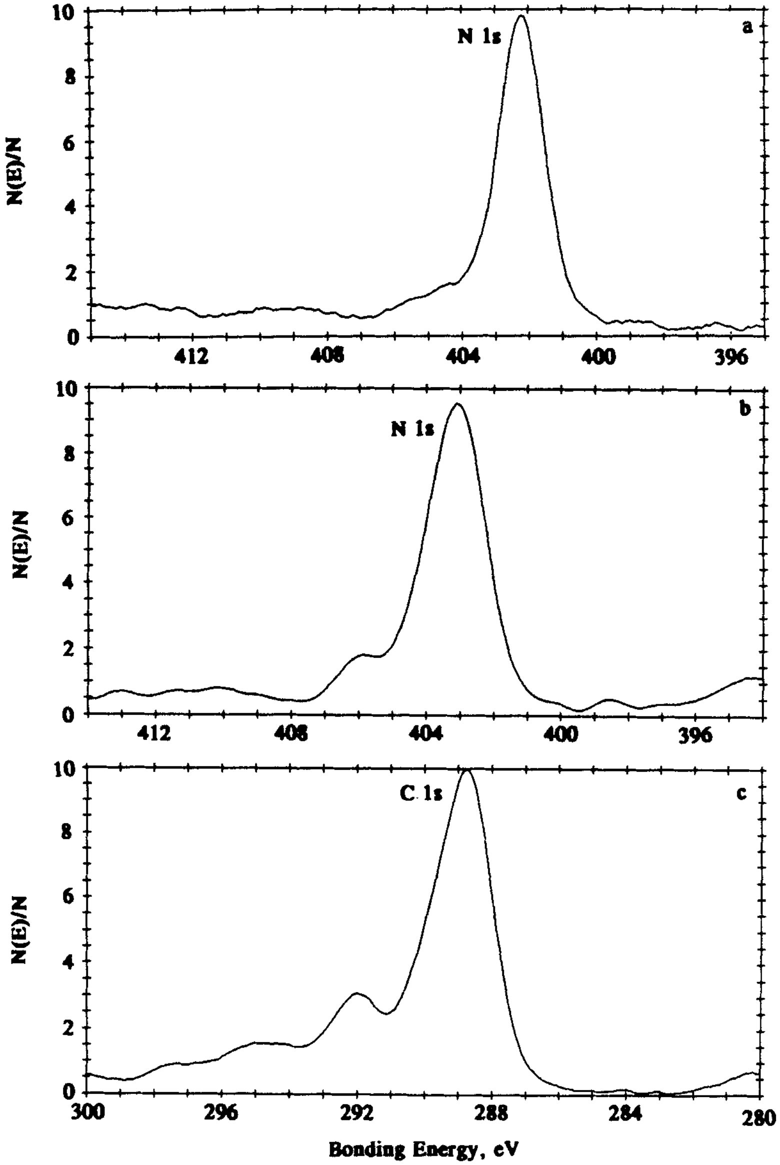


FIGURE 1 XPS multiplex (relative counts per second [N(E)/E] versus binding energy) recorded using Mg-Kα (1253.6 eV) of: a) py-surface baked at 100°C for 1 h after soaking in a 1% solution (by volume) of 2-trimethoxylsilyethyl-2-pyridine for 2 minutes at room temperature; b) and c) EDTA-surface baked at 110°C for 1 h after soaking in a 1% solution (by volume) of N-[3-trimethoxysilypropyl]-ethylenediaminetriacetic acid for 2 minutes at 60°C

silylethyl-2-pyridine solution (see Figure 1a). The atomic ratio of nitrogen to silicon, which characterizes the molecular concentration of organosilane on the surface, increases approximately from 1:9 to 1:5 when the time of immersion increases from 2 min to 45 min.

In the case of the treatment with N-[3-trimethoxysilylpropyl]-ethylenediaminetriacetic adic, no measurable reaction took place in 45 minutes at room temperature.

At 60°, significant silanization was found to occur in 2 min. with the N1s peak detected at 403.3 eV (see Figure 1b). Besides C1s (288.6 eV) from *adventitious carbon* a shoulder at higher bonding energy (291.8 eV) was observed. The binding energy of the peak is characteristic of carboxylate C (see Figure 1c). The ratio (silane molecule/Si) increases from 1:22 to 1:12 as the reaction time increases from 2 min to 45 min at 60°.

There are no elements present to distinguish the silane from the glass surface in the case of OTS-surfaces so that methods other than XPS have to be employed to demonstrate the silanization. As discussed later, contact angle measurements and the behavior of treated surfaces with respect to inhibition of peeling made it obvious that silanization occurred.

It should be mentioned that all XPS peaks show a shift to higher energy caused by charging during the experiments. For example, the peak C1s from *adventitious* C was found at 288.1 eV; Si 2p at 106.1 eV; and O1s 535.0 eV on a py-surface. The shifts may vary slightly from surface to surface. No corrections were made to the observed binding energies.

Inhibition of Peeling of Bi_2S_3 Thin Films

The occurrence of peeling of films deposited on the untreated substrates depends upon a number of variables. These include the cleanliness of the substrate, the deposition time and post-deposition treatment. Films peel more readily from uncleaned surfaces than from clean ones; the longer the depositon time, the thicker the films become and the more likely they are to peel; and films deposited on glass substrates by the "double dip" method must be dried quickly after rinsing in order to inhibit their peeling.[3]

During the preparation of Bi_2S_3 thin films described on the experimental section, it was observed that the films which were grown on untreated surfaces for a period of 5 h or longer, in "single dip" deposition, peeled to varying degrees when rinsed. For films deposited on EDTA-modified surfaces, peeling occurred after 3.5 h deposition. In contrast to this, films deposited on the other modified surfaces which remained in the chemical deposition bath for as long as two days showed no signs of peeling. The thickness of the film grown in "single-dip" deposition was usually no more than 0.18 μm[11] and the chemical bath for production of Bi_2S_3 thin films appeared to be depleted after approximately 7 h of deposition. Thus extended exposure to the solution did not appear to promote peeling provided that the thickness of the film did not increase.

To grow thicker films, "double-dip" depositions were employed. All slides were coated in the first chemical bath for 4 hrs. At this stage, all of the films remained intact except for those deposited on EDTA-modified surfaces. The slides were then transferred to the second bath and the deposition was allowed to proceed for additional 2 to 6.5 h. The films deposited on untreated glass substrates, which were grown for a total time of 6 to 10.5 h, peeled as soon as they were rinsed with distilled water. In contrast, no peeling occurred with any of the films deposited up to a coating period of 10.5 h on SH-surfaces and OTS-surfaces while those on py-surfaces and NH_2-surfaces were found to resist peeling during a coating period of up to 9 h. The appearance of the thin films deposited on the different surfaces of

TABLE II

The appearance of Bi_2S_3 thin films deposited on modified surfaces

Substrates	Deposition time (hour)							
	2.0	3.5	5.0	6.5	6.0	7.5	9.0	10.5
Glass surface	I	I	I	I/D	D	D	D	D
SH-surface	I	I	I	I	I	I	I	I
NH_2-surface	I	I	I	I	I	I	I	D
py-surface	I	I	I	I	I	I	I	D
OTS-surface	I	I	I	I	I	I	I	I
EDTA-surface	I	I	D	D	D	D	D	D

[a] The substrates were treated in a solution of organosilanes for 15 minutes. I-intact, D-detach; I/D-sometimes intact and sometimes detatch.

substrates are summarized in Table II. Thus, it has been found that treatment of the glass surface with a silicone reagent able to form a covalent bond to glass at one end, and possessing an appropriate terminal functional group, results in a significant diminution in undesired peeling. The ability to inhibit peeling follows the order:

$$\mathrm{SH} \sim \mathrm{OTS} > \mathrm{NH_2} \sim \mathrm{py} > \mathrm{glass} > \mathrm{EDTA}.$$

The resistance to peeling of treated films was accompanied by obvious improvements in the physical character of the deposited material. Electron scanning microscopy showed that Bi_2S_3 thin films on SH-surfaces were more homogeneous than those on untreated surfaces. In the latter case, after 4 hours of deposition, the particles were irregular in size with large and variable spacing between them (Figure 2e). Similarly prepared films on SH-surfaces yielded surface particles which were more uniform in appearance and more evenly spread over the film (Figure 2f). Films deposited for shorter times (10 minutes and 30 minutes) were also examined in order to study their appearance at earlier stages of growth (Figures 2a–2d). The SH-surface shows more extensive nucleation after 10 minutes and more uniform surface coverage after 30 minutes than the untreated surface does. Because of the aggregation of individual particles after deposition for longer times the average particle diameter and its distribution were measured only for films of 10 minutes deposition time. The electron micrographs (Figures 2a and 2b) were enlarged to 8" × 10" in size and a rectangular grid placed over the prints. The mean linear dimension of the particles in one direction,[14] d, the standard deviation of that mean, sd, and the number of particles measured, n, were: untreated surface, $d = 47$ nm, $sd = 1$ nm, $n = 305$; SH-surface, $d = 33$ nm, $sd = 1$ nm, $n = 287$. Other micrographs were taken and they support these observations. The EDTA-

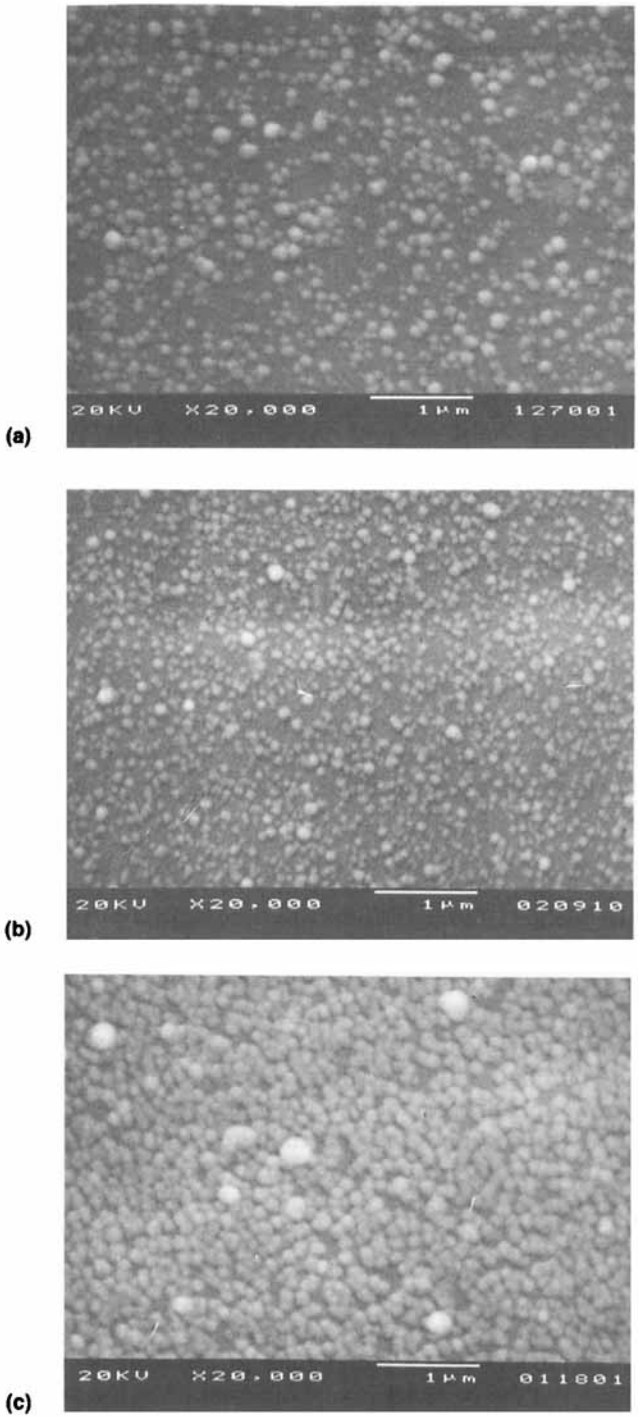


FIGURE 2 SEM of Bi_2S_3 thin films. a) 10 min deposition on untreated glass substrate; b) 10 min deposition on SH-surface; c) 30 min deposition on untreated glass substrate; d) 30 min deposition on SH-surface; e) 4 h deposition on an untreated glass substrate, and f) 4 h deposition on SH-surface

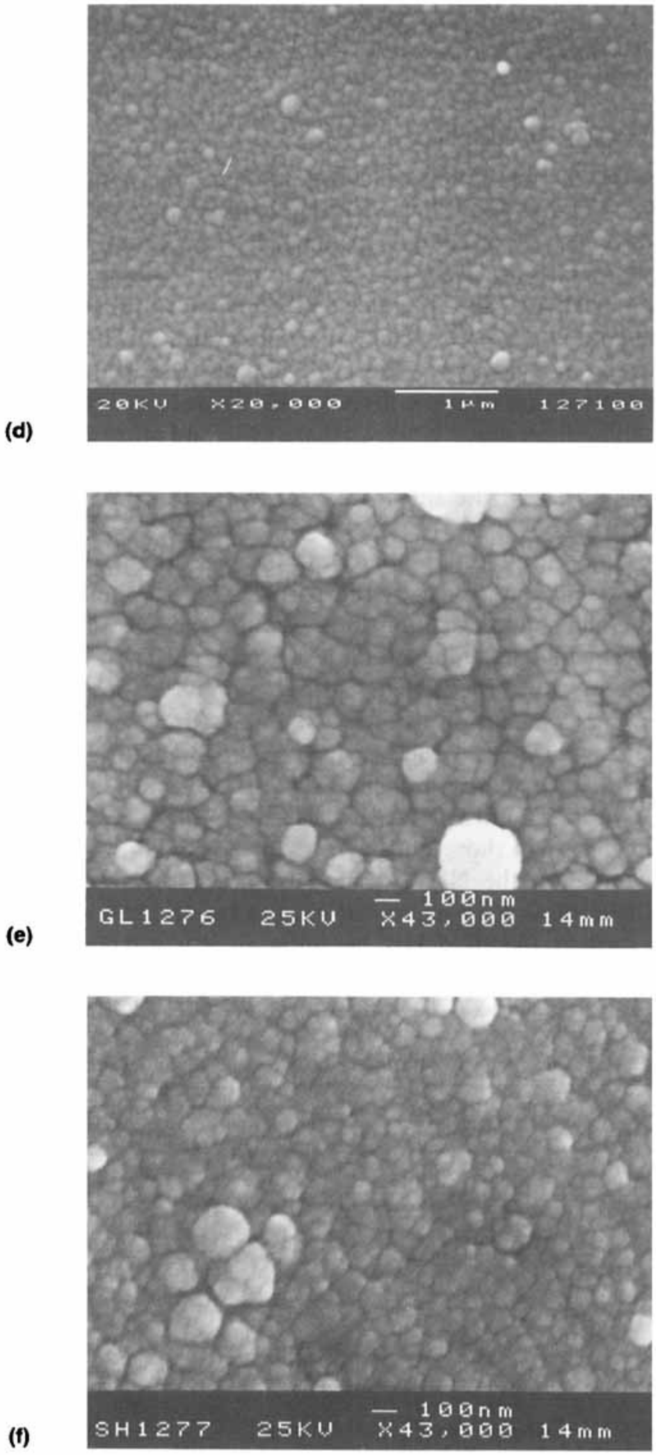


FIGURE 2 (*Continued*)

surface resembles the untreated glass surface, the OTS-surface resembles the SH-surface and the NH_2-surface falls between these extremes.

Surface Properties of the Substrate

The mechanism of the growth of a metal sulfide film on a glass substrate has been studied previously.[15,16] It has been suggested that in alkaline solution the metal ion first forms the hydroxide. Hydroxyl groups on the glass surface function as seed nuclei on which the metal sulfide crystals grow.

When the surface is treated in a manner which enhances the bonding between the material to be coated and the surface of a substrate, the film attachment is improved. There is strong evidence, as described below, that Bi-S chemical bonds are formed in the preparation of Bi_2S_3 films on the SH-surface. However, there is no evidence for a similar interaction between these films and other modified surfaces for which peeling has been inhibited. This suggests that in addition to bond-forming capability, other properties of the substrate are involved in the peeling phenomenon.

In order to investigate the binding ability of a surface to Bi(III), the following experiments were carried out. Each of the surfaces was immersed in a Bi(III) solution for 25 min. The solution composition was the same as that of a chemical deposition bath except that no thioacetamide was added. The modified surfaces used in the experiments were those that had been immersed in a silane solution for 15 min. The atomic concentrations of Bi, Si and X (the characteristic element of silane when there was one) on each surface were obtained by means of XPS analysis and the results are summarized in Table III. Bismuth concentrations on the SH-surface (Bi/Si, 0.22) and EDTA-surface (Bi/Si, 0.14) were approximately two to four times higher than those on the OTS-surface (Bi/Si, 0.06) and 20 to 40 times higher than those on the NH_2-surface (Bi/Si, 0.005) or py-surface (Bi/Si, 0.007). On the surface of a clean untreated glass substrate, the ratio (Bi/Si) was 0.15 while on this surface, baked at 110° for an hour, it was 0.05. It appears that

TABLE III

The contact angle and the concentration of bismuth and modified surfaces*

Substrate	Contact angle	Silane molecule/Si	Bi/Si
Glass-surface	spread		0.15 (unbaked) 0.037 (baked)
SH-surface	44	0.15	0.22
NH_2-surface	58	0.11	0.007
py-surface	52	0.12	0.005
OTS-surface	67		0.06
EDTA-surface	spread	0.037	0.14

The modified surfaces were those which were treated in a silane solution for 15 minutes.

there are only relatively weak interactions of Bi(III) with NH_2- and py-surfaces, considerably stronger interactions with the others, and little correlation with the inhibition of peeling. For example, the EDTA-surface has a high [Bi/Si] ratio but is the least effective with respect to inhibition of peeling. This can be interpreted as follows. The EDTA-silane possesses three terminal coordinating groups. It is reasonable to invoke a process which involves strong coordination of one Bi(III) to three carboxylate groups of one EDTA unit and thus a high [Bi/Si] ratio. But, because the charge on Bi(III) is neutralized locally, sulfide ions will not be bound firmly to the EDTA-surface and the Bi_2S_3 film, without special points of attachment, peels easily.

To examine another surface property of these substrates, contact angles with water were measured and the results are summarized in Table III. Based on the values of the contact angles, the order of hydrophobicity was: OTS $>$ NH_2 $\sim$ py $>$ SH $>$ glass $\sim$ EDTA. As expected, OTS-surfaces to which long hydrocarbon chains were bonded were found to be the most hydrophobic among these surfaces. The value of contact angle on the OTS-surfaces after 15 min treatment, which were used in the deposition of Bi_2S_3 thin films, is 67° and it increases with the immersion time in the silane solution. With the immersion times of 45 min, 60 min, 240 min, the contact angles are 78°, 98°, and 103° respectively and thus the OTS-surfaces used in the deposition were not in full coverage. Full coverage monolayers on SiO_2 surfaces were previously prepared under other conditions: on glass surfaces coated with OTS, an advancing contact angle of 112° was obtained[12] and on oxidized silicon surfaces treated with OTS, angles of 104° (dry substrate) and 114° (hydrated substrate) were measured.[17]

The glass surface and ionic EDTA-surfaces appear to be highly hydrophilic. The surfaces of bismuth sulfide thin films were also examined. The contact angle for thin films prepared under different conditions of chemical deposition (0.15 $\sim$ 0.3 μm in thickness) fell in the range of 69° to 74°. Earlier work on crystal surfaces of heavy metal sulfides has shown that they are strongly hydrophilic[18,19] but that the introduction of organic materials such as oleic acid greatly increases their contact angles with water.

Except for the SH-surfaces, in which there is evidence of the formation of Bi-S chemical bonds, it was found that the larger the contact angle, the longer the films can be kept in the chemical deposition bath without peeling. During the formation of the very first layer of Bi_2S_3 on the surface of a substrate one can imagine that there may be a competition between water molecules and Bi_2S_3 to cover the surface. A surface which is less easily wet by water is favored to form a uniform layer with numerous nuclei and thus to resist peeling. The fact that the OTS-surface inhibits peeling is interesting because such a surface is coated with non-polar hydrocarbon residues. However, it was observed that Bi_2S_3 films deposited on OTS-surfaces could be easily wiped off of the slides with a dry cotton tissue. In contrast to this, all of the films deposited on other surfaces could not be removed in this manner. This observation clearly illustrates the importance of making a distinction between peeling and adhesion of thin films. The forces between the non-polar OTS-surfaces and the BI_2S_3 crystallites are likely to be weaker than those between the other, more polar surfaces but the flexible nature of the long hydrocarbon chains surface also make them less likely to peel as the film thickness increases.

Evidence for Bi-S Bond Formation

The results suggest that SH-surfaces are the most effective in inhibiting the undesirable phenomenon of peeling and that the Bi_2S_3 films deposited on this surface possess superior homogeneity. It is proposed that the initial step in the process of Bi_2S_3 deposition on SH-surfaces involves the formation of a glass—O—$Si(CH_2)_3$—S—Bi bond. Supported by the fact that SH-surfaces show a strong ability of binding Bi(III) this hypothesis, was tested as follows.

To a solution containing 2.5 ml of 0.5 M bismuth nitrate solution (described in the experimental section), 2 ml of triethanolamine/water (1:1 by volume) and 20 ml of deionized water was added three drops of the organosilane. A heavy, bright yellow precipitate formed immediately. The precipitate was separated by filtration, rinsed with deionized water followed by methanol and air-dried. Chemical analysis gave 14.74% S; 32.46% Bi. This corresponds to a S/Bi ratio of 2.96 which is in excellent agreement for the reaction between one mol of Bi(III) and three mol of reagent I. The C/S ratio is 3.85, presumably because of the ease of hydrolysis of $Si\text{-}OCH_3$ groups and the possibility of polymerization of the hydrolyzed products.

It is known that organothiols react with various kinds of metal ions, including Bi(III), to yield mercaptides and these reactions have been used to determine thiols quantitatively.[19] The colors of bismuth mercaptides were found to vary from colorless to yellow to orange depending on the nature of the thiols used. Hence, it is proposed that when SH-surfaces are immersed in the Bi_2S_3 deposition bath, the formation of glass—O—$Si(CH_2)_3S$—Bi bonds is very likely. These then serve as seed nuclei upon which Bi_2S_3 crystals grow. Such a scheme offers an explanation of the inhibition of peeling and the greater homogeneity of the films. Reagents II, III, and IV were also tested in the same fashion as Reagent I but no precipitate with Bi(III) was observed.

CONCLUSION

The glass surfaces modified by treatment with organosilanes bearing various functional groups affect the peeling of Bi_2S_3 thin films. The ability to prevent the peeling of Bi_2S_3 thin films by organosilanes having different functional groups followed the order: SH $\sim$ OTS $>$ NH_2 $\sim$ py $>$ untreated glass $>$ EDTA. Both the SH- and EDTA-surfaces can react with Bi(III). The difference between the behavior of an SH-surface and an EDTA-surface may be attributed to the difference that in the latter case one Bi(III) can be neutralized by three carboxylate groups of a single EDTA unit and that consequently sulfide ions are not attracted to the surface, whereas only one bond is formed between Bi(III) and S in the SH-surface. When no specific interactions existed between Bi(III) and the modified surface, such as for NH_2-surfaces, py-surfaces and OTS-surfaces, it was found that, the larger the contact angle between water and the surface, the greater the resistance to peeling.

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