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Materials for Passive Radiative Cooling

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Executive summary

This project aimed to develop passive cooling devices, based on preferential heat rejection through the atmosphere. The project was split into two parts: preparation of a selective heat emitter (the Peruvian group) and preparation of a solar shield (to prevent heating by solar radiation during the day (Israeli group).

Emitter. Initial results with silicon oxynitride emitters made by spray pyrolysis were encouraging. Attempts to scale up the emitters were more problematic due to irreproducibillty over large areas, in particular believed due to differing water contents of the emitters. Useful small emitters were fabricated and tested.

Shield. Two different types of shields were made. One consisted of semiconductor films (Te, PbS and PbSe) deposited on polyethylene foils by simple chemical methods. These shields gave good solar blocking behavior. The PbS appears to be the best in the respect that solar radiation is reflected as much as it is absorbed, resulting in less heating. Another type consisted of white pigments (the best were ZnO and ZnS) prepared in the polyethylene foils, which scattered a considerable amount of the solar radiation, again preferable than absorbing. Preliminary experiments were carried out towards the end of the project to combine both types together – this is believed to be the optimum configuration.

Small devices were made using the emitters from the Peruvian group and the shields from the Israeli group. Efficient heat blocking during the day and slight (1.5 °C) cooling during the night were obtained from these devices. Due to the relatively high humidity, which lowers cooling efficiency, an artificial atmosphere was constructed to test the emitters and shields during a 4 month visit of one of the Peruvian team (Alcides Lopez) to Israel. One of the Israeli investigators (Gary Hodes) spent a week in Lima and gave some seminars on film deposition as well as discussing the project.

Research objectives

To fabricate, using simple techniques, selective emitters and solar shields (as described above) for passive cooling devices and to incorporate them into actual devices. This necessitated optimizing spectral characteristics of the materials over a wide spectral range (from 300 nm to 13 μm). Certain materials may be known, a priori, to potentially have the desired properties; however, any one material can exhibit very different spectral properties depending on a number of parameters, such as particle size and stoichiometry (or impurity levels). Thus we often investigated different techniques of making the (ostensibly) same material. Only a small amount of work has been carried out on practical passive cooling and studies on the shields have used vacuum evaporation techniques rather than the simple solution-based chemical methods used here.

Results

Brief background. Passive cooling refers to the preferential emission of radiation in the 8-13 μm window region, resulting in cooling of the emitting surface. The dry atmosphere is relatively transparent to this window region; therefore the emitted radiation can be directly radiated through the atmosphere into space, which acts as a cold sink. That is, the passive radiator (at close to ambient temperatures) is the source and cold space is the sink in a Carnot cycle. Ideally, the radiator (or emitter) should selectively emit radiation in the window region.

While this concept can work well at night (assuming a relatively dry atmosphere), the solar energy input during the day, which is normally much more than that radiated out, would cause heating. To prevent this, a shield is needed to cover the radiating surface in order to block the solar radiation (and also to prevent convective mixing between the cold radiator and the warmer surrounding air). The required properties of such a shield are (ideally) complete blocking of the solar radiation (300-3000 nm) and complete transmission of the IR window region (8-13 μm).

This project was involved both with the selective emitter (studied by the Peruvian group) and the shield (studied by the Israeli group).

The selective emitter (W. Estrada and M. Horn, UNI, Peru)

Research Accomplishments

In order to obtain selective emitters (black in the atmospheric window of 8 - 13 μm, and reflective outside), different fabrication methods to obtain silicon oxide based coatings on stainless steel and on aluminum substrates have been studied. The results obtained in the laboratory on small samples till the end of 1997 looked quite promising, as reported in earlier annual reports. The selectivity of the samples was estimated by looking at the IR spectra of the samples.

In 1998 we tried to reproduce the best samples on a bigger scale, in order to be able to make a prototype radiative cooler of the size of about 1 m^2, as foreseen in the project. First we had a lot of difficulties to reproduce on a larger scale our best results obtained before on small samples (2,9 x 6 cm^2). Apparently the IR spectra were sensitive to small variations in the fabrication procedure and the composition of the initial chemicals used, as well as on the following heat treatment. In particular, the absorbance in the IR range below the atmospheric window was sensitive to the heat treatment, caused probably by different contents of water molecules in the coating.

At the beginning of 1999 we could get finally a sample of 10 x 10 cm^2, with similar IR spectrum as the best small samples before. However, exposing it, together with other reference samples, to the night sky (in Lima), we could not measure a significant cooling effect one (as expected from theoretical calculations). In reality, a reference black body sample reached lower temperature. (We did not expect a big cooling effect, as the humidity of the air in Lima is quite high.)

We started then to evaluate quantitatively the emittance of the samples inside and outside the atmospheric window. For this purpose, we considered as a reference a black body emitter at 0 °C (273 °K). A blackbody at this temperature emits 314,9 W/m^2, from which 93, 3 W/m^2 are inside the atmospheric window. As our IR spectrometer permits only to measure in the range of 3 - 30 μm, including 272,6 W/m^2, we have an error of up to (314,9 - 272,6) / 314,9 = 13 % in the calculations of the emittance outside the window.

The results were quite disappointing. The results for our best samples were:

1. On aluminum substrate:

inside the window:

71,7 W/m^2, resulting in an emittance of $\varepsilon = 71,7 / 93,3 = 0,76$

outside the window (3 - 30 μm):

100,2 W/m^2, ε = 100,2 / 179,3 = 0,55

2. On steel substrate:

inside the window:

63,1 W/m^2, resulting in an emittance of ε = 63,1/ 93,3 = 0,67

outside the window (3 - 30 μm):

80,5 W/m^2, ε = 80,5 / 179,3 = 0,45

3. On aluminum evaporated on glass substrate:

inside the window:

43,2 W/m^2, resulting in an emittance of ε = 43,2 / 93,3 = 0,46

outside the window (3 - 30 μm):

37,2 W/m^2, ε = 37,2 / 179,3 = 0,20

Whereas the qualitative inspection of the IR spectra, as reported earlier, shows an apparently good absorption (low reflection) in the atmospheric window, the quantitative calculations give an emittance inside the window of only ε = 0, 76, on aluminum substrate, and ε = 0,67, on steel substrate.

While we obtained a clear selectivity of our samples, $\varepsilon_{inside} / \varepsilon_{outside}$ = 0,76 / 0,55 = 1,38 (Al substrate), 0,67 / 0,45 = 1,48 (steel substrate) and 0,46 / 0,20 = 2,3 (evap. Al/glass substrate), in order to get good cooling, it is particularly important to have a high emittance (at least 0,8) inside the window. Our low values explain the low cooling effect observed.

We currently are analyzing the cause of those effects; it seems clear that the substrate is playing a critical role and probably (as preliminary tests show) they are not the appropriate ones. The results show that evaporated Al on glass substrate shows better behaviour; so we are going to continue working in this procedure in order to improve the quality of the substrate.

Conclusions

Whereas we have developed different techniques to fabricate selective infrared emitting coatings, with reasonable values of selectivity ($\varepsilon_{inside} / \varepsilon_{outside} = 2.3$), the best values obtained for the emittance inside the atmospheric IR window are too low to observe good cooling effects.

We will continue to work on this subject in order to improve the emittance inside the window. The first step is to find an ideal substrate and for this aim we are going to make more testing using vacuum evaporated Al glass substrates.

The shield (G. Hodes and D. Cahen, Weizmann Institute of Science)

We have investigated a number of directions to improve shield properties in order to approach this ideal situation as closely as possible. These are.

1. Optimization of the substrate for the shield.
2. Introduction of optical scattering materials *into* (as opposed to deposited onto) the shield substrate (pigmented polyethylene foils).
3. Films of absorbers/reflectors and of antireflection coatings deposited onto the substrate.
4. Testing of the shields for passive cooling.

Note on spectral measurements. All FTIR spectra are direct (specular) transmission(reflection) while the UV/vis/near IR spectra are diffuse transmission and reflectance, unless noted otherwise. The diffuse spectra are the more relevant ones for the shield properties, since it is the total and not just the direct amount of radiation which is important. It is only in the last year of the project that we obtained a spectrophotometer which could measure diffuse radiation, and measured or remeasured relevant spectra.

1. Substrate.

Thin polyethylene foils or films are the only practical substrate for the shield at present. Other materials either absorb too strongly in the window region or, as for high bandgap semiconductors, are not feasible in large areas. We studied several different types of polyethylene, both commercial and ones we prepared ourselves by polymerization. While the ones we prepared ourselves were slightly more transmissive between 9 and 10 μm, probably due to lack of additive impurities which occur in commercial samples. the

difference was small and was offset by the difficulty in preparing relatively large areas compared to the ease of obtaining commercial films.

Other in-house prepared films tested by us included high density polyethylene and films with copolymers. The rationale in both cases was to improve the rigidity of the films, thereby preventing convection losses due to movement of the shield caused by wind. The high density polyethylene showed unacceptable absorption in the window region. The copolymer, while slightly poorer than the normal low density samples in terms of transmission, was somewhat more rigid. While promising, we decided, because of the marginal difference, to use the commercial film for reasons of ease in obtaining the films.

Fig. 1 shows the FTIR transmission spectrum of a 50μm commercial polyethylene film, which can be referenced against the shields described in this report. The average transmission in the window region is ca. 80%.

2. Pigmented polyethylene foils.

Ideally, the solar radiation should be completely reflected, since absorbed radiation is converted to heat somewhere in the system. Highly-reflecting materials, such as metals, reflect by virtue of their high free charge carrier concentration, and for the same reason, reflect also in the window region. Fairly high reflectivity (although much lower than for metals) can be exhibited by materials with a high dielectric constant, such as Te and PbS(e). However, a third alternative is to use materials in a finely-divided form which scatter short wavelengths much more efficiently than long wavelengths (Rayleigh scattering efficiency is inversely proportional to the fourth power of the wavelength).

Using this principle, we have prepared pigmented polyethylene foils containing 5% (by weight) of the scattering pigment. The pigments investigated were: ZnO; ZnS; Te; TiO_2; carbon; C_{60} carbon fullerene; antimony oxide (Sb_2O_3).

The two most promising materials were ZnS and ZnO, with Sb_2O_3 also showing some promise. Fig. 2 shows the FTIR transmission spectra and UV/vis/near IR transmission and reflectance spectra of two samples using ZnS and ZnO. The ZnS(O) powder was mixed with melted high density polyethylene HDPE) at 210°C. The product was pressed into a film at 165°C at 10,000 psi. for 3 mn. Ideally, low density polyethylene should exhibit better window region transmission; however, at this stage, it was easier to make homogeneous samples with HDPE.

The average transmission in the window region is ca. 60% for both samples (we do not consider the somewhat better transmission of the ZnS sample to be important at this stage; it may be due simply to variations in processing). The transmission drops toward the solar region, reaching zero at ca. 400 nm for both materials. The ZnS is appreciably better (less transmitting) than the ZnO over the solar region. For example, at 800 nm, the transmission of the ZnS is 28% while that of the ZnO is 43%. The loss in transmission is

due to reflection and not absorption, a desirable property for a shield. The better reflection of the ZnS may be due to its somewhat higher dielectric constant.

It should be noted that, for the FTIR (window region) measurements, since the samples are quite far from the detector of the spectrophotometer, the measured transmission will actually be *lower* than the effective transmission when used in a device. Thus the transmission values given should be taken as minimum values.

3. Films.

Tellurium

Te is one of the most ideal materials (optically speaking) for the shield. It is (theoretically, for pure, intrinsic material) transparent in the window region and should block the entire solar region. Also, because of its large dielectric constant, it should have a high reflectance in the solar region. Reflectance losses in the window region are appreciable but can be lowered by antireflection coatings. While vacuum evaporation is a standard method to deposit such films, we have considered non-vacuum techniques in preference in keeping with the demands of simplicity of preparation.

Initially, we considered decomposition of tri-butylphosphine telluride in solution to form Te films. While elemental Te did form in these solutions, it formed homogeneously throughout the solution rather than as a film on a substrate as required. We therefore discontinued this approach.

The second, and much more successful approach, was by decomposition of electrochemically-formed H_2Te. This method was based on earlier attempts to deposit CdTe films by chemical solution deposition. While CdS and CdSe can be easily deposited by this technique, the corresponding deposition of CdTe has never been accomplished. We were studying the use of H_2Te for this purpose. We devised an electrolytic cell to form H_2Te in situ (this gas is very unstable and readily decomposes to Te and H_2). The H_2Te was formed cathodically using a Te cathode (formed by electrodeposition of Te on Ti from a TeO_2 solution), a Pt anode and a separated cell with an electrolyte of 50% H_3PO_4 in an ice bath (the latter to minimize H_2Te decomposition). We noticed that the Tygon tubing connecting the electrolytic cell to the Cd-solution blackened, presumably due to decomposition of the H_2Te to Te catalysed by the Tygon surface. We therefore exploited this observation, initially by rolling a polyethylene foil into the Tygon tubing and passing H_2Te through the tube, which resulted in deposition of a black Te film on the polyethylene.

Subsequently, we devised a set-up where the electrogenerated H_2Te, together with N_2 (99.999%) as a carrier gas, passes into a wash borttle which contains the rolled up polyethylene substrate (size?). The non-decomposed H_2Te + N_2 then passes into a second wash bottle of aqueous NaOH (to absorb the excess H_2Te) and a third bottle of aqueous $CuSO_4$ solution (as an indicator to be sure that no H_2Te escaped).

The Te films formed were not very homogeneous (particularly thicker films), and contained many patches of visibly thinner deposit. We therefore looked for methods of improving the homogeneity of these films. We found in the literature a technique to improve the adhesion of chemically deposited semiconductor films on various plastics [P. Pramanik and S. Bhattacharya, J. Mater. Sci. Lett., 6, 1105 (1987)]. This technique was based on immersion of the polyethylene in aqueous $KMnO_4$ solution until a thin brown film (probably MnO_2) formed on the polyethylene. This film was then removed and the chemical solution deposition was carried out on the treated polyethylene. We found that better results were obtained if the MnO_2 layer was not removed. This layer did not reduce the window region transmission in any way and therefore was not detrimental in any way for our purposes. It did reduce the visible solar transmission considerably, mainly by absorption and to a small degree by reflection (fig. 3a, spectrum B). This characteristic may be somewhat advantageous or disadvantageous, depending on the properties of the film to be deposited on the MnO_2. In practice, it is not expected to make an appreciable difference. Therefore overall, this film does not much affect the optical properties of the shield but improves the adhesion of subsequently-deposited layers.

Fig. 3 shows the UV/vis/near IR transmission (a), reflection (b) and FTIR transmission (c) spectra of a Te film on MnO_2/polyethylene deposited by this technique. The transmission is ca. 60% in the IR window region, compared to ca. 85% for the bare polyethylene (the greater part of the loss in transmission is due to reflection). This is a sufficiently high transmission for practical applications. The transmission drops to a fraction of a percent over the entire visible spectrum and well under 10% even in the longer wavelengths of the solar spectrum. Most of the blocking arises from absorption in the Te film; reflection over the UV/vis/near IR range is typically between 10-20%, although occasionally reflectances up to 40% have been obtained.

Regarding the environmental aspects of this deposition technique, H_2Te is very poisonous and there may be a problem with its use in a manufacturing facility. On the other hand, in our laboratory set-up, it is generated <u>in situ</u> in a closed system, and we found no trace of the gas in the outlet exhaust (the solution of $CuSO_4$ at the gas outlet showed no sign of blackening - which would be clearly visible if even traces of H_2Te were present).

<u>PbSe</u>

Mainly due to its low bandgap (0.27 eV; 5 μm), PbSe is a potential alternative to Te. If thick enough, it should block the solar spectrum but, if intrinsic, be transparent in the window region. Also, it has a high dielectric constant which implies high reflectivity. Of particular importance in our case, we have considerable experience in deposition of PbSe using the simple technique of chemical solution deposition and can control its optical properties in the visible/near IR region. The films are made by mixing aqueous solutions of

lead acetate, a complexing agent (most often trisodium citrate or KOH) and sodium selenosulphate, and leaving the polyethylene substrate in this solution for typically a day at various temperatures. Since we subsequently found that PbS possessed better characteristics for a shield, only a brief discussion of the results on PbSe is presented here.

Fig. 4a shows an FTIR spectrum (The and R) of two chemically deposited PbSe films using two different complexants. The window region transmission is high (>70%). UV/vis/near IR spectra are shown in fig. 4b. In general, most of the blocking is due to absorption rather than reflection.

PbS

We had earlier found that PbS, a material which we originally had considered as a shield material, was found to absorb in the window region, and therefore we concentrated on PbSe, which we found to be more transmissive. However, in view of the somewhat less toxic nature of PbS compared to PbSe, its lower cost, and the fact that, in theory, it could be as transmissive as PbSe in the window region, we continued to carry out experiments on this material. Subsequently, we found that transmissive samples could be made with properties superior to those of the best Pbse films made up to now. Although we have much less experience with the chemical deposition of PbS compared with PbSe, the advantages noted above were sufficient to convince us to shift the study from PbSe to PbS. The overall deposition technique was similar to that used for PbSe, only using thiourea as a sulphur source in place of selenosulphate as a Se source.

Fig. 5(a) shows a FTIR transmission spectrum of a PbS film on polyethylene. The window transmission is ca. 75% - a very respectable value for a shield. The UV/vis/near IR transmission and reflectance spectra are shown in fig. 5(b). The transmission over most of the IR region is ca. 25%, falling to a very low value in the visible. Of particular interest, the reflectance is high, reaching almost 60% in the solar IR region (although clearly much lower in the window region as can be inferred from the high transmission in this region). Therefore, much of the blocking behaviour in the solar IR region is due to reflection which switches over to predominant absorption in the visible region. This film was ca. 70 nm thick.

PbS films we had studied in the first year of the project were not very transmissive in the window region. The difference in IR transmittivity between those films and the present ones is probably related to doping of the latter (which introduces free charge carriers, thereby causing IR absorption and reflection). We do not as yet know what the reason is for this difference; it may be due to an impurity in the former films. While the difference is of scientific interest, we were unable to investigate it further in the framework of this research.

ZnS

We have deposited ZnS films by chemical deposition, the intention being to use them as antireflection coatings to maximize transmission in the window region. This is based on the principle of index matching; since reflection increases as the difference in refractive indices of the two media at an interface increases, by placing a material with an intermediate refractive index between the two media, reflection decreases. ZnS has a refractive index less than that of Te and more than that of air (the two media in this case). While films of ZnS could be deposited on polyethylene which exhibited the characteristic UV absorption of the wide bandgap ZnS and were basically transparent in the window region, as expected, when deposited on Te-on-polyethylene, the transmission of the film in the window region *decreased* compared with bare Te (from ca. 60% to ca. 38%). While it is likely that this is not an intrinsic effect (it depends strongly on film thickness and morphology), we decided that the potential advantage of the antireflection coating was less than improving the blocking behaviour of the shield and did not continue this direction further.

4. Devices.

Some simple devices were constructed and tested. Two types of devices were studied: those used under normal atmospheric conditions and those used in an artificial atmosphere.

For the normal atmospheric tests, initial tests were carried out in a polystyrene box with the shield taped to the box. However, most of the subsequent results were obtained using a perspex box, (11 x 7 x 3.7 cm internal dimensions), with a top frame to hold the shield which could be screwed into the box. This box was placed inside an insulating expanded polystyrene box. A Temptale temperature data logger, small enough to fit inside the box, was placed at the bottom. The temperature vs time could be downloaded from the Temptale to a computer.

The first property which we measured was the blocking capacity (prevention of heating without an emitter). Fig. 6 compares the temperatures inside a box with a shield of Al metal and another box with a Te/MnO_2/ polyethylene shield with the outside ambient temperature over a 24 hour period. Both the Te and Al shields prevent the boxes reaching the high ambient temperatures measured during the daytime. In fact, although the Al should block the solar radiation completely while the Te allows a small fraction through, the temperatures in the Te- shielded box were lower overall than those in the Al-shielded box. The former performed slightly poorer than the latter early in the day but considerably better later on. This suggests that the better overall performance of the Te is because of thermal conduction through the Al resulting in heating inside the box. This result shows the good blocking behaviour of the Te shield.

The next stage was to measure the passive cooling during the night. Here the shield was not needed to block sunlight but to allow thermal (window) radiation to be emitted from

the box and to prevent convective mixing between ambient and inside of the box. Fig. 7 shows the cooling effect. It is small (maximum 1.5 °C) but clear. The reference polyethylene obviously gives the lowest temperature at night, but the Te shield is only slightly inferior and certainly better than the control Al (black body) cover. The small cooling effects were attributed to the high humidity in this region (>60% humidity is usual, sometimes approaching 100%), and passive cooling will not be very effective under such climatic conditions. Under other conditions, experiments were carried out using the same device on three different nights in three different climates. Two of these (Rehovot - 94% humidity and Jerusalem - 75% humidity) gave no measurable cooling while the third (Yatir in the desert - 32% humidity) gave a maximum 1.2°C difference.

Because of the high humidity, we investigated the possibility of testing devices in an artificial atmosphere. We used the vacuum chamber of a vacuum evaporator and constructed a steel top plate with a hollow copper fixture into which liquid nitrogen (LN_2) could be poured from outside the top plate. The dimensions of this fixture was 8.8x8.8x1.5 cm (for the LN_2 container) with a plate of 11x9.3x0.2 cm attached to the bottom. This bottom copper plate acted as the "sky" or sink at a temperature of the LN_2 (in practice, a bit higher). The cooling device was placed at the bottom of the evaporator; a distance of 15 cm from the sink. Fig. 8 shows a schematic diagram of the setup.

Fig. 9 compares the temperature vs. time using a selective emitter (silicon oxynitride, prepared in Lima) and a black body (Al with a covering of soot formed by smoking the Al) in the cooling device with a blank polyethylene shield. The room temperature, external to the bell jar, was 25°C. The temperature of the Al outside the box gives, to some extent, a reference temperature of the belljar, caused by LN_2 cooling. However we are aware that this temperature is actually cooler than the backgrounbd temperature since the Al itself acts as an emitter, if not very efficient (a true measurement of temperature in the belljar is not trivial; a thermocouple placed in the bell jar can itself act as an emitter. An IR-blocking shield between thermocouple and cold plate should help, but up to now, has not been dependable). The Al emitter inside the box actually cools slightly less than that outside, showing that the the latter, with no polyethylene to slightly block the mid-IR, does act as an emitter. The selective emitter (which is only 80% of the area of the Al) cools better and a "black body works the best. It is known that a black body will cool faster than a selective emitter but should not reach as low an ultimate temperature. From these experiments, a cooling of at least 5°C was measured (and probably larger as explained above). We should note that these experiments were carried out with a sensitive measuring system (thermocouple attached to the preamp of a microvoltmeter and then to a recorder). Early experiments on the artificial atmosphere did not use the preamp and were not very reliable. It should be noted that the vacuum required for these experiments should be ca. 20 mTorr or lower. The experiments on the artificial

atmosphere were carried out mainly during a four month visit of Mr. Alcides Lopez, from the Peruvian group, to the Weizmann Institute.

Overall conclusions.

Three materials have been shown to possess suitable optical properties for a shield to be used in a passive cooling device – Te, PbSe and PbS. These materials can be deposited on polyethylene using simple chemical (non-vacuum) methods. It is difficult to state which of these materials will be ultimately best.

Good scattering shields have been made by incorporating ZnS into the polyethylene substrate (pigmented shields). While these shields are not sufficiently blocking by themselves, a combination of pigmented polyethylene with a Te or PbS layer may give the optimum performance. Some preliminary experiments were carried out in this direction with high vis/near IR reflectivity but still insufficient window trnasmission. Testing of actual devices was problematic, presumably due to the high humidity in this region. To overcome this problem, an artificial atmosphere was designed and used with better results. A follow up of these experiments would involve illuminating the device, fitted with a shield, in the vacuum with a solar simulator and measuring the resulting cooling.

Figure captions

Fig. 1. FTIR reflection spectra of 50 mμ commercial polyethylene film.

Fig. 2. (a) Vis/near IR transmission and reflection spectra of polyethylene films containing 5% ZnS or ZnO. (b) FTIR transmission spectra of the same ZnS and ZnO films.

Fig. 3. (a) Vis/near IR transmission spectra of polyethylene (A), polyethylene + Mn-O film (B) and polyethylene + Mn-O + Te (C). (b) reflection spectra of the same samples. (c) FTIR transmission spectra of the Te film (B) compared with bare polyethylene (A).

Fig. 4a. FTIR transmission and reflection spectra of PbSe deposited from two different baths (nitrilotriacetate – NTA; trisodium citrate – TSC). 4b. Vis/near IR transmission and reflection spectra of the films.

Fig. 5a.. FTIR transmission and reflection spectra of PbS film, prepared by chemical solution deposition, on polyethylene. 5b. Vis/near IR spectra of the film.

Fig. 6. Temperatures measured over a 24 hour period in an insulated box with an aluminium shield, a Te/MnO_2/polyethylene shield, a bare polyethylene cover and the outside ambient temperature.

Fig. 7. Temperature measured at night inside an insulated box with a black body radiator and an Al (black body) cover, a bare polyethylene shield and a Te shield.

Figure 8. Schematic diagram of the artificial atmosphere.

Figure 9. Temperature with different emitters in the artificial atmosphere. Al inside the box; Al outside the box; Si-O-N; smoked Al.

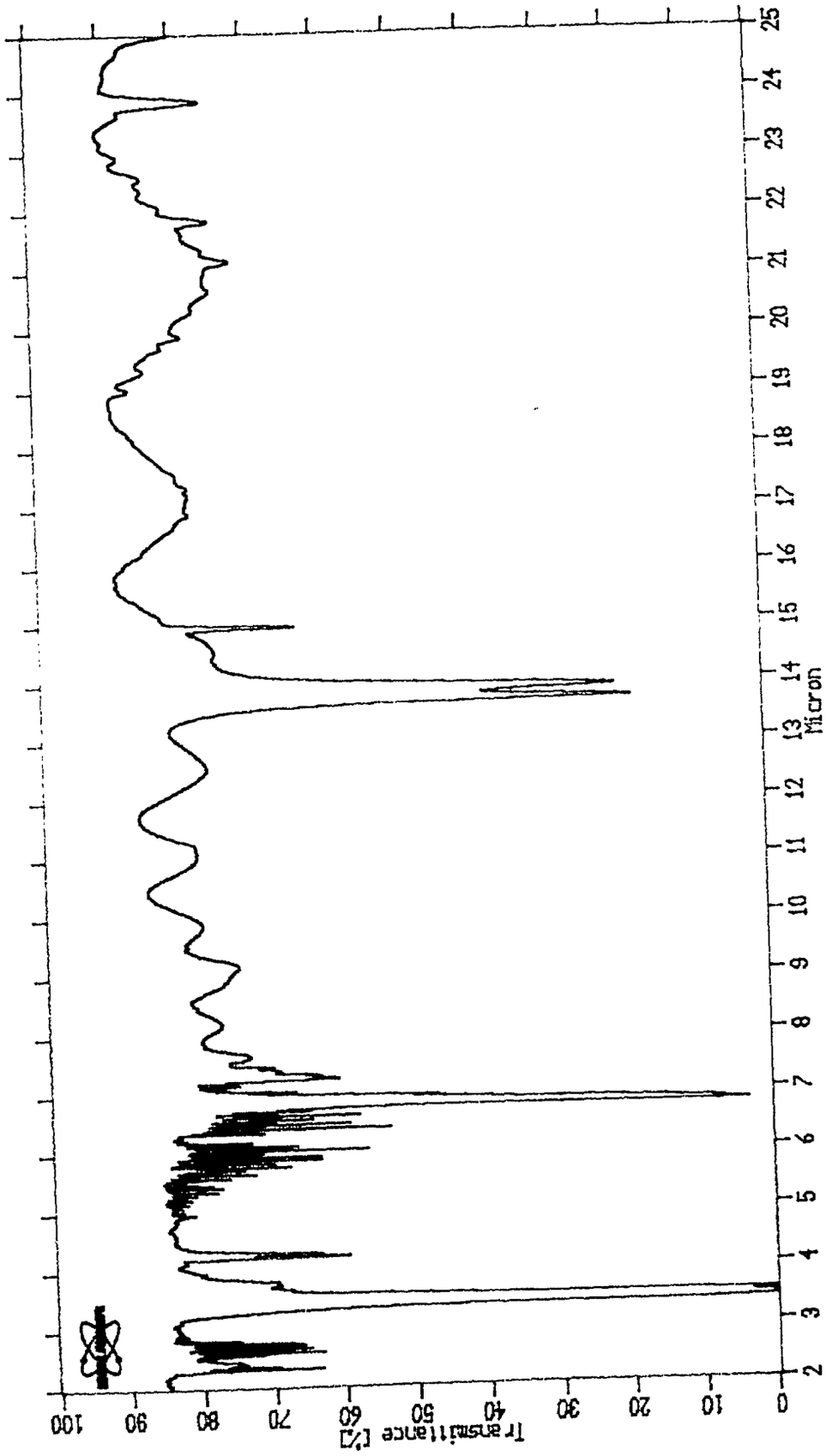
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Fig 1

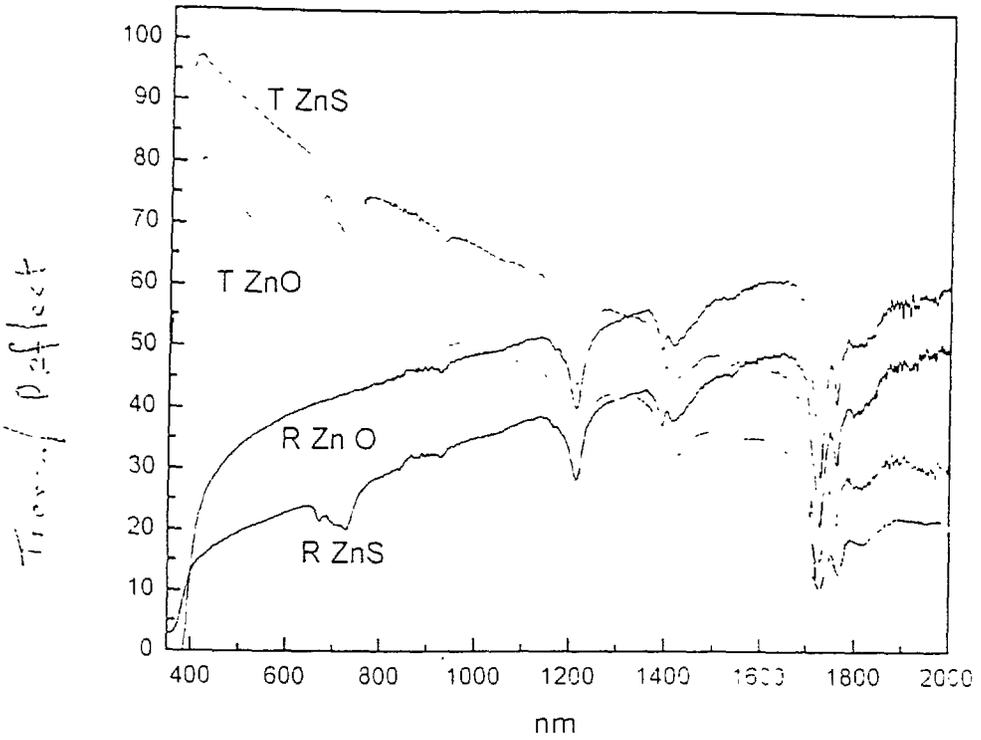


Fig. 2a

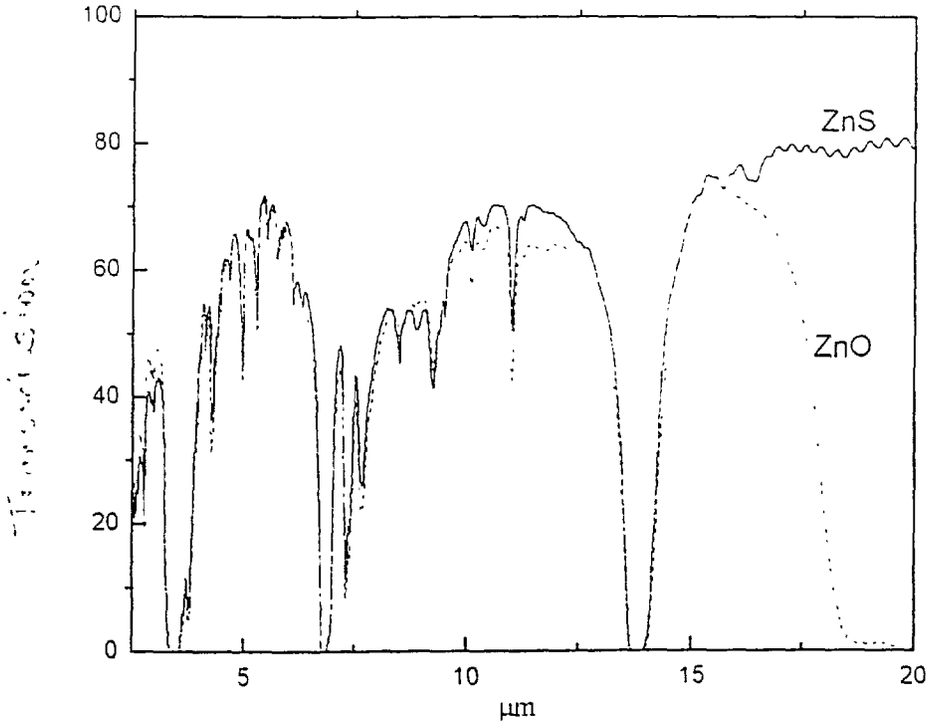


Fig. 2b

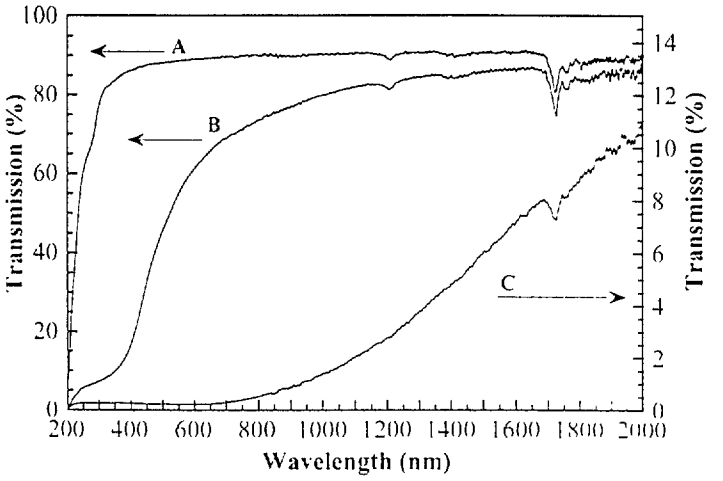


Fig. 3a

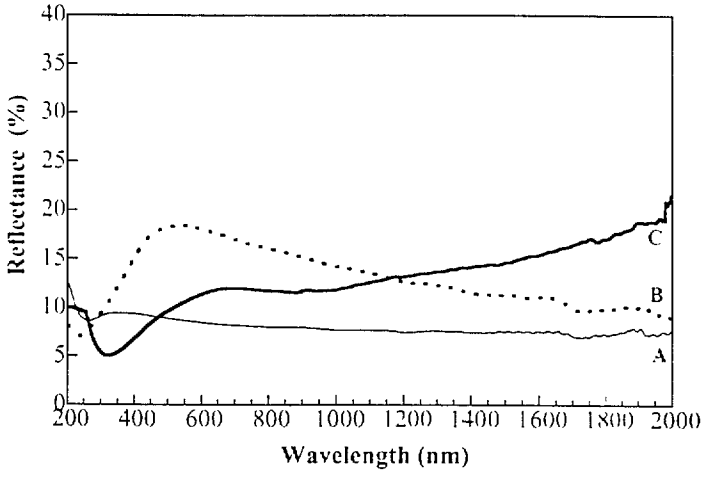


Fig. 3b

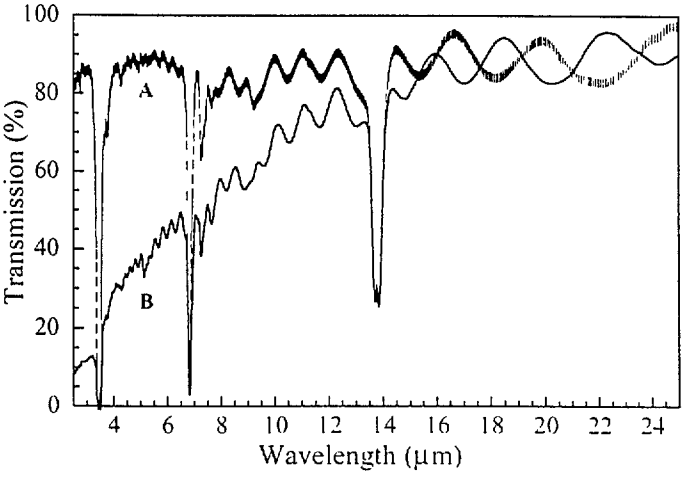
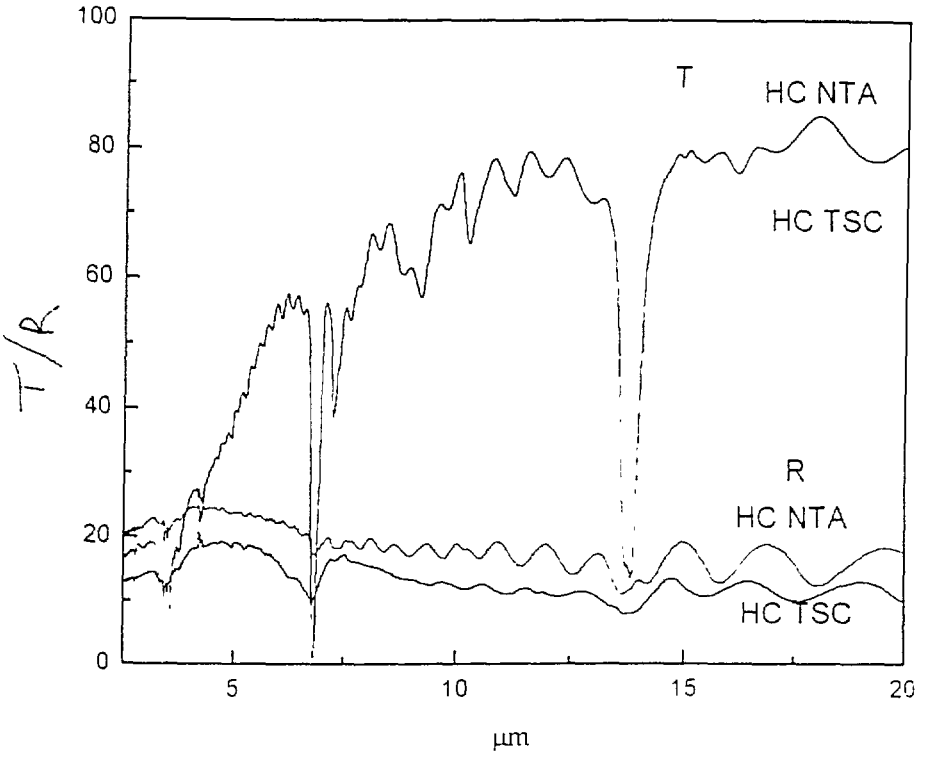


Fig 3c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µm

Fig 4a

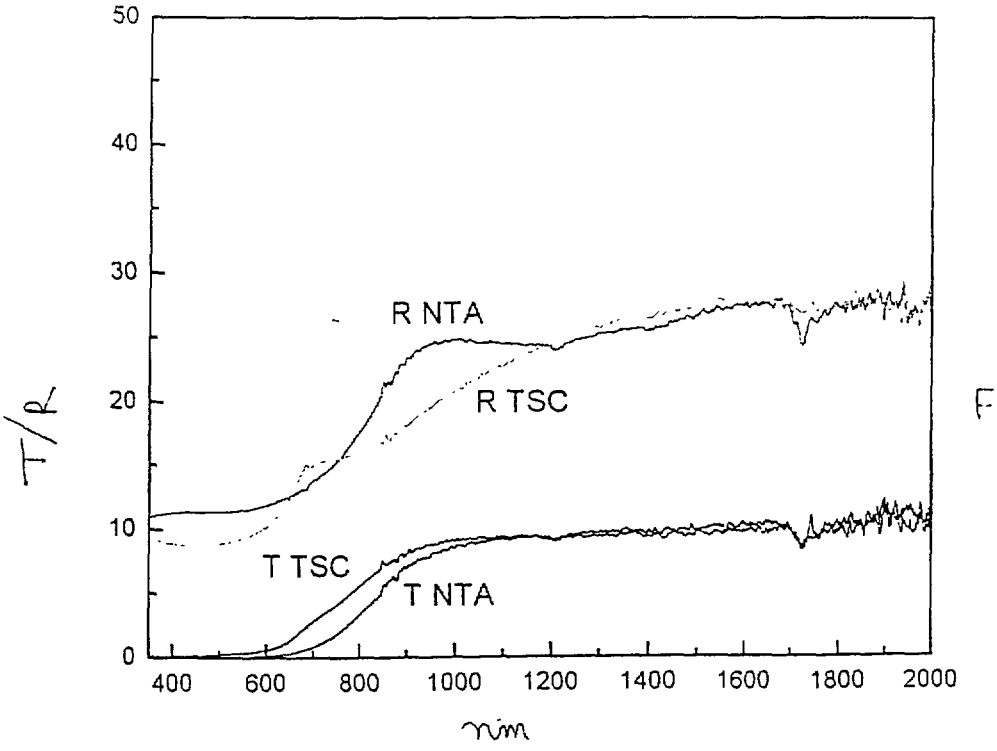
50
40
30
20
10
0
T/R
R NTA
R TSC
T TSC
T NTA
400
600
800
1000
1200
1400
1600
1800
2000
nm

Fig 4b

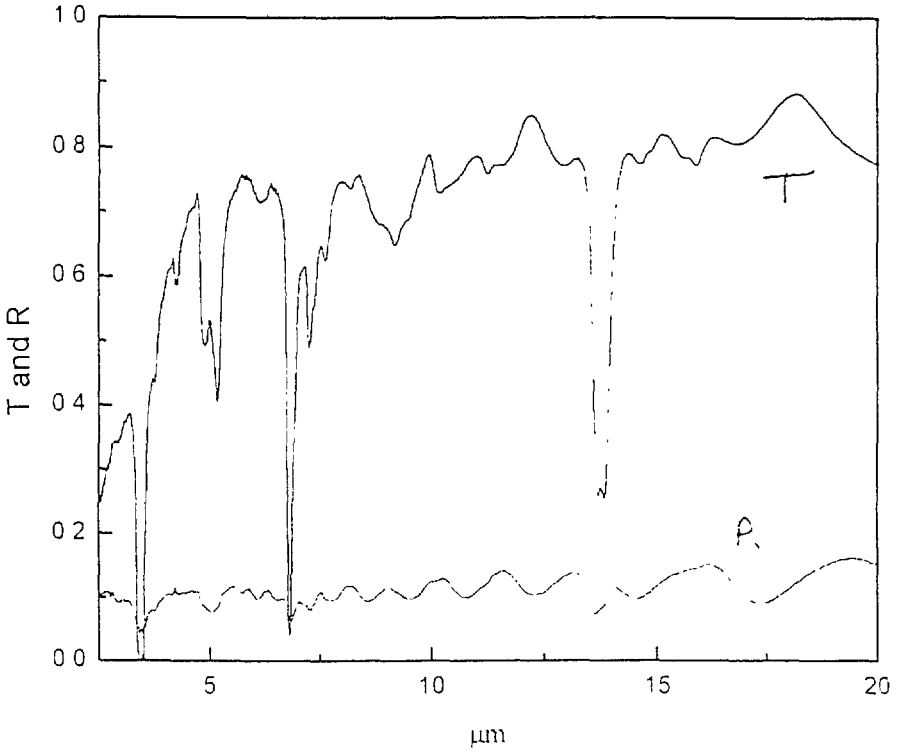
1 0
0 8
0 6
0 4
0 2
0 0
T and R
5
10
15
20
µm
T
R

Fig. 5a

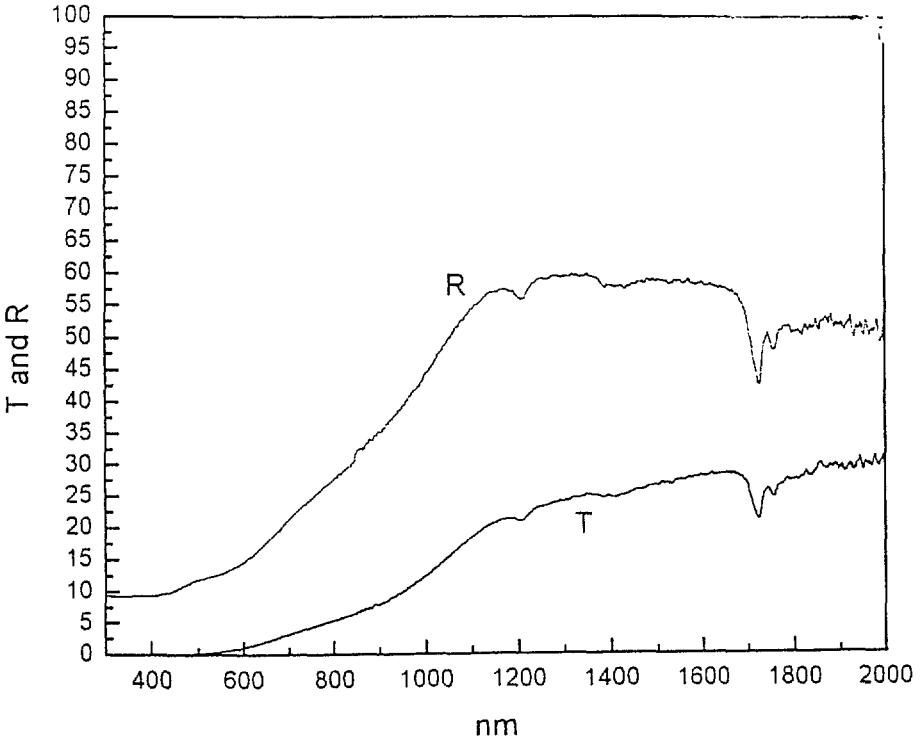
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
T and R
400
600
800
1000
1200
1400
1600
1800
2000
nm
R
T

Fig. 5b

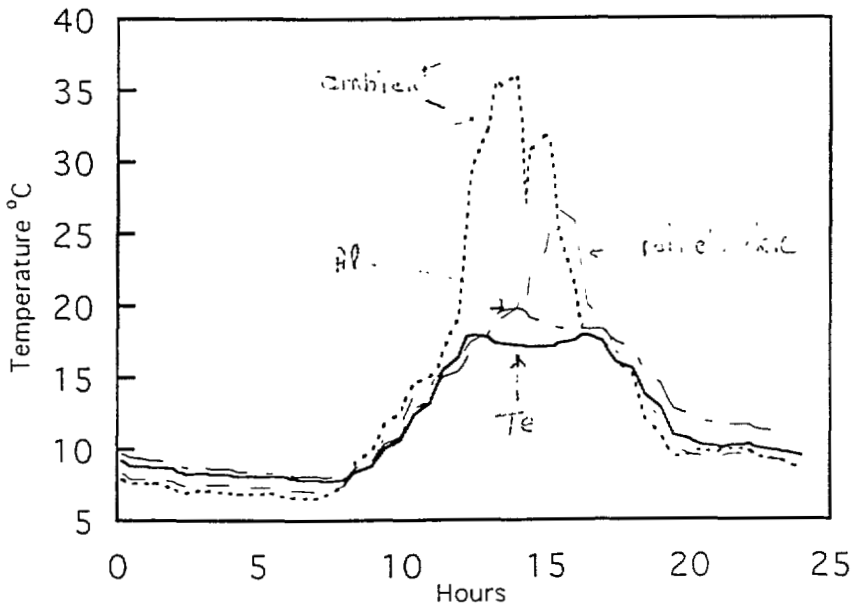
40
35
30
25
20
15
10
5
Temperature °C
0
5
10
15
20
25
Hours
Te

Fig 6

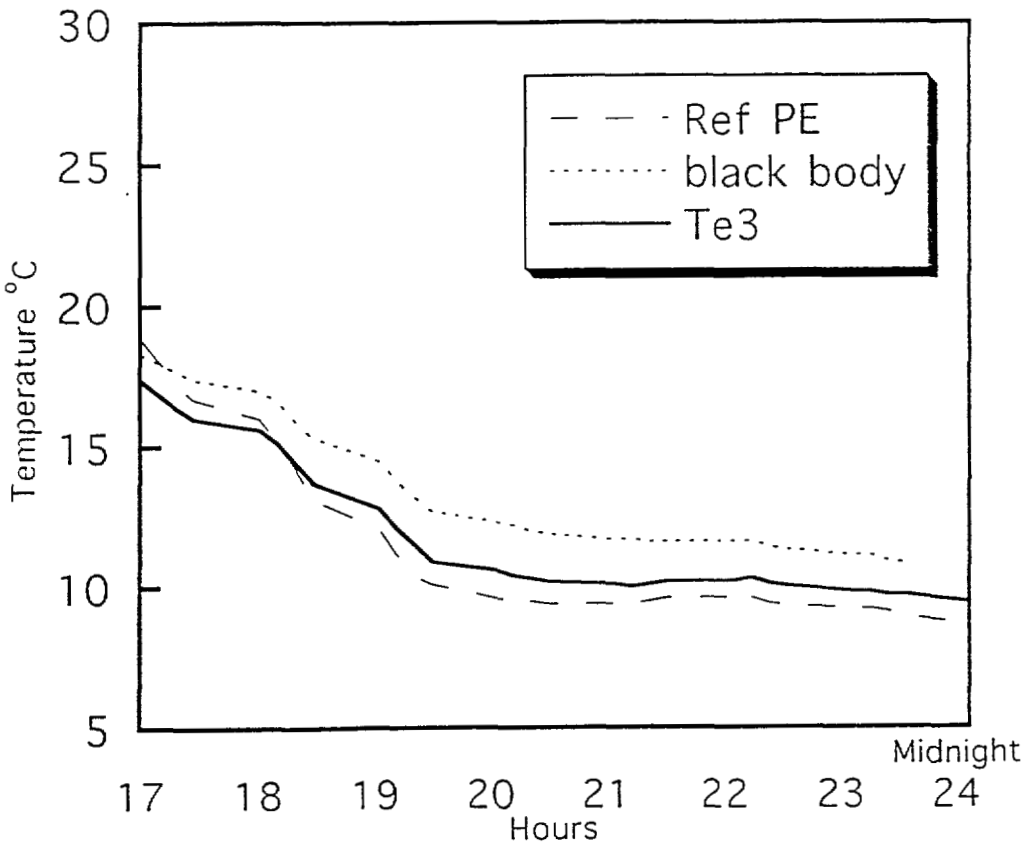
30
25
20
15
10
5
Temperature °C
Ref PE
black body
Te3
Midnight
17
18
19
20
21
22
23
24
Hours

Fig. 7

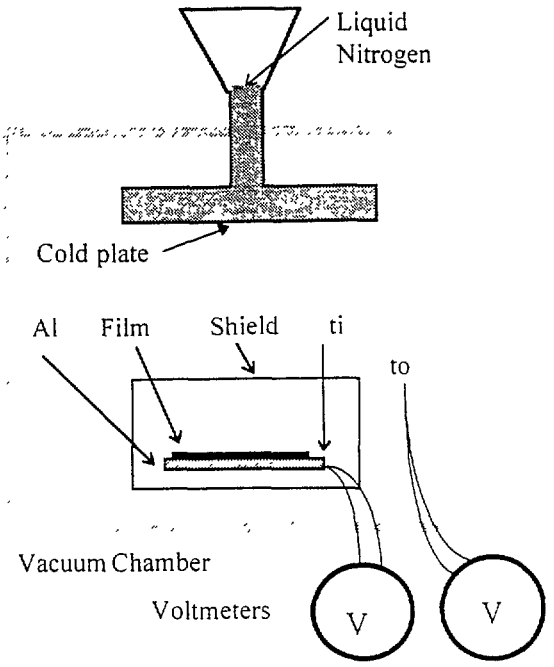
Liquid
Nitrogen
Cold plate
Al
Film
Shield
ti
to
Vacuum Chamber
Voltmeters
V
V

Fig. 8

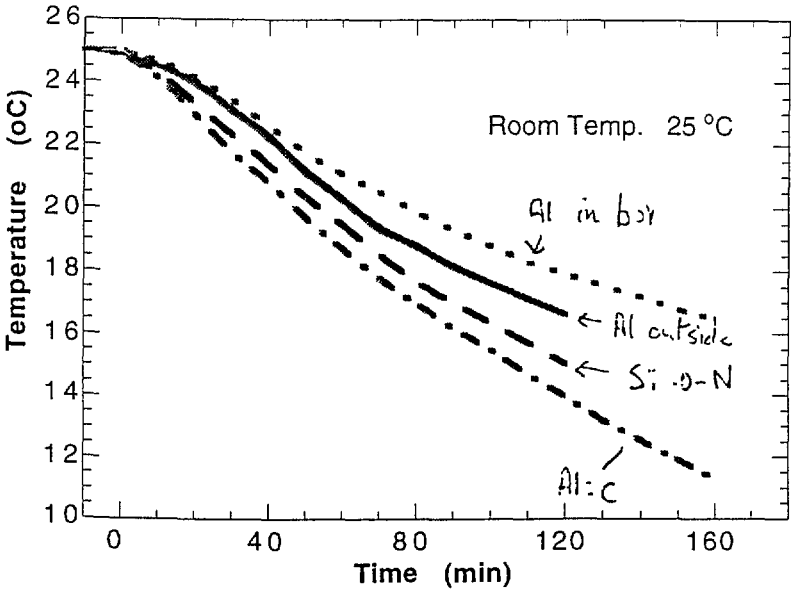
Room Temp. 25 °C
Al in box
Al outside
Si-O-N
Al:C
Temperature (oC)
Time (min)
26
24
22
20
18
16
14
12
10
0
40
80
120
160

Fig. 9

Impact, relevance and technology transfer

The Peruvian group has improved their capability, both in terms of equipment (spray pyrolysis) and know-how in film preparation. One of their MSc students spent four months at the Weizmann Institute and developed skills there additional to those used in his home institution. Seminars on semiconductor film deposition were given by one of the Israeli investigators at the Peruvian university.

It is planned to continue the shield studies, combining the qualities of the pigmented and thin film-coated shields. This will be done at a modest level since it will now be non-funded work.

Project activities

1. Visit of MSc student (Alcides Lopez) in Israel for four months. Learnt methods of film deposition used in the Weizmann group. Emphasis of his work was on an artificial atmosphere set-up to test the various samples.
2. Seminars by Gary Hodes in Lima on semiconductor film deposition.
3. Publications:

Deposition of Tellurium Films by Decomposition of Electrochemically-Generated H_2Te: Application to Radiative Cooling Devices (Thin Solid Films, in press).

Thin Semiconductor films as shields for radiative cooling applications. Manuscript in preparation.

Project productivity

We succeeded in constructing small devices with good heat blockage and a small cooling effect. A number of different materials were identified as good shield components. An artificial atmosphere was constructed which should be useful for measurements of the properties of materials for passive cooling.

We were not able to make large devices due to scale-up difficulties. The cooling effects were smaller than hoped for, probably due to humidity.

Suggested future work

Combination of pigmented and film-deposited shields is the most obvious direction based on our results, as described.

Thin Solid Films – In press

Deposition of Tellurium Films by Decomposition of Electrochemically-Generated H_2Te: Application to Radiative Cooling Devices

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[2] Centre for Data Storage Materials, Coventry University, Coventry, CV15FB, UK.

Abstract

The preparation of homogenous, large area thin layers of tellurium on thin polyethylene foils is described. The tellurium was formed by room temperature decomposition of electrochemically generated H_2Te. Pre-treatment of the polyethylene substrates with $KMnO_4$ to give a Mn-oxide layer was found to improve the Te adhesion and homogeneity. Optical characterization of the layers was performed using UV/VIS/NIR spectroscopy. Such coatings have favorable characteristics for use as solar radiation shields in radiative cooling devices. The simplicity of generation of the very unstable H_2Te was also exploited to demonstrate formation of size-quantized CdTe nanocrystals.

Keywords. Tellurium films, passive radiative cooling, hydrogen telluride, CdTe quantum dots.

Introduction

Tellurium, with a low bandgap of 0.32 eV (ca. 4 μm), is one of the most promising materials for a shield in a passive radiative cooling. In radiative cooling, thermal radiation in the 8-13 μm region is transferred from the radiator through the earth's atmosphere (which, in the absence of clouds, is transparent in this region - the atmospheric "window") - to the (ideally) 4 K heat sink of space, causing cooling of the radiator [1]. While this radiative cooling effect can occur efficiently at night when there is little energy input into the system, heating by absorption of solar energy during the day would normally swamp the cooling effect. For this reason, a shield is required that serves the dual purpose of preventing the solar radiation from reaching the radiator and preventing convection between the radiator and the ambient, both of which would result in heating of the cold radiator. This shield must obviously also be transparent to the window region (8 - 13 μm) in order to allow cooling to occur.

Low bandgap intrinsic semiconductors are obvious candidates for this purpose since their low bandgap implies blocking of solar radiation, but they are normally transparent in the mid-to-far IR region; free carrier absorption in the IR reduces this transparency in doped semiconductors. Theoretical calculations have shown that thin layers of Te have the appropriate characteristics [2]. Te layers have been prepared for this purpose by low vacuum evaporation [3, 4].

Our aim was to devise a simpler method of depositing Te which does not require a vacuum, based on the expectation that radiative cooling is most likely to be used, at least initially, in developing countries where economy and simplicity of fabrication are important factors. In this paper, we describe deposition of Te films onto polyethylene foil by room-temperature decomposition of electrochemically generated H_2Te. Polyethylene is a suitable substrate for

these experiments as it is reasonably transparent, in the form of thin foils, in the IR window region.

Experimental

Preparation

Because of the high instability of H_2Te, it was preferable to generate it in situ as required, and it was generated essentially according to the method described in ref. 5. This method was based on the electrolytic reduction of a Te cathode in aqueous solution. Although this method was described over 80 years ago, and despite its simplicity, it does not appear to have been exploited to any extent.

Deposition of Te cathode.

The Te cathode (ca. 1 x 3 cm) was prepared by cathodic electrodeposition of Te onto a titanium substrate from an aqueous 0.15M TeO_2 solution in KOH (pH of 11-12) at a current density of 10mA/cm^2 at room temperature for 24-48 hr and using a carbon counter electrode. This gave a layer of ca. 0.2 mm (measured by weighing the substrate before and after deposition); considerable hydrogen evolution occurred at the cathode, resulting in the low plating efficiency.

H_2Te generation.

A glass U cell, with a glass frit separating the two sides of the cell, was used for the H_2Te generation. The Te cathode was placed in one side and a Pt anode in the other. The electrolyte was a 50% aqueous phosphoric acid solution. The glass frit was used to avoid decomposition of the H_2Te by oxygen generated at the Pt anode. An inert gas flow (99.999 nitrogen) was used to degas the catholyte and also to act as a carrier for the H_2Te (total gas flow rate of approx. 5 ml/min) to minimize its residence time in the cell. In order to further minimize H_2Te decomposition in the cell, the whole setup was immersed in an ice bath. High currents (ca. 0.3 A) were necessary to generate H_2Te within a reasonable time. This is probably because the initially formed H_2Te dissolved in the electrolyte, as well as the slow continuous decomposition of the H_2Te in the cell. Although we did not measure the efficiency of generation of H_2Te, it is low, due both to this decomposition and to the large amount of hydrogen co-generated with the H_2Te.

Preparation of the polyethylene substrate.

Low density polyethylene foil substrates, ca. 50 μm thick, were cut to different sizes ranging from 2 x 3 cm^2 up to 10 x 10 cm^2, cleaned with detergent and rinsed well with water. Direct deposition of the tellurium on the polyethylene substrate tended to give blotchy, non-homogeneous layers. Good homogeneity, reproducibility and also better adhesion of the Te was obtained by permanganate treatment of the polyethylene [6]. The polyethylene sheets were immersed in a 10% $KMnO_4$ solution for several days, resulting in a thin, brown manganese oxide layer.

Te deposition on the polyethylene.

The H_2Te + N_2 (+H_2) gas mixture was led from the electrolysis cell into a glass wash bottle-type vessel, using the minimum of interconnecting tubing, in particular rubber tubing (the H_2Te decomposes as it passes through the tubing, slowly on glass and much faster on Tygon, leaving a film of Te on the inside of the tubing). The polyethylene substrate was wrapped around a thick glass tube or vial (somewhat smaller in diameter than the glass vessel) and placed concentrically inside the vessel so that the surface of the polyethylene was exposed to the gas flow. The outlet of the glass vessel was led into a wash bottle of aqueous NaOH, to absorb any unreacted H_2Te and then to another wash bottle containing $CuSO_4$ solution as an extra absorber and also an indicator for the very poisonous H_2Te: black Cu-Te forms if free H_2Te is present at that stage.

There is an induction time of up to 5 min, depending on the electrolysis current, where no visible change occurs on the polyethylene. This is probably due to decomposition of the initially formed H_2Te by remaining traces of oxygen in the electrolyte and by dissolution of the H_2Te in the electrolyte. The final thickness of the Te films depends on the time of deposition. Typically, we find that 30min at a current of 0.3 A results in a Te thickness of ca. 0.1 μm. On completion of the deposition, the setup was flushed out with nitrogen to remove remaining H_2Te by absorption in the wash bottles.

Characterization

All FTIR spectra are direct (specular) transmission reflection while the UV/VIS/NIR spectra are diffuse transmission and reflectance. FTIR transmission spectra were performed on a Bruker IFS-66 FTIR spectrophotometer over a wavelength range of 2-25 μm (4500-500 cm^{-1}). Visible and near IR spectra were performed, over the range from 0.2 - 2 μm using a Jasco V-570PC spectrophotometer fitted with an integrating sphere. Spectra were recorded at room temperature, with a scanning speed of 100 nm/min.

Powder x-ray diffraction (XRD) spectra of the films were recorded on a Rigaku RU-200B Rotaflex diffractometer operating in the Bragg configuration using Cu K_α radiation. The accelerating voltage was set at 50 kV with a 150 mA flux. Scatter and diffraction slits of 1° and a 0.6 mm collection slit were used.

Scanning Electron Microscopy (SEM): A JEOL JSEM 500 scanning electron microscope operating at 20 kV was used for the characterization of the films.

Results and Discussion.

Structure of deposit.

XRD (fig. 1A) showed that the deposit was hexagonal Te. The XRD peak widths were identical to the instrument broadening (ca. 0.04°), which means that the crystal size was at least 100 nm. Since the Te thickness was typically 100 nm, as noted above, this means that the polyethylene was covered with essentially one layer of crystals. No diffraction pattern from the Mn-O film could be observed.

SEM micrographs of the Mn-O coated polyethylene (a) and a Te deposit on the Mn-O/polyethylene (b) are shown in fig. 2. The typical lateral particle size of the Te is several hundred nm.

Optical spectra of the films.

In order to be able to compare the characteristics optical proportions of different films, we define some optical functions. We define integrated transmitted intensity (T_{Sol}), and integrated reflected intensity (R_{Sol}), for UV/VIS/NIR and for the atmospheric window. We follow the definition of Granqvist *et.al* [7] and define the solar reflectance by averaging the spectral reflectance of the films over the solar spectrum.

$$R_{Sol} = \frac{\int_{\lambda_1}^{\lambda_2} R(\lambda)W(\lambda)\partial\lambda}{\int_{\lambda_1}^{\lambda_2} W(\lambda)\partial\lambda}$$

$W(\lambda)$ = AM 1.5 solar spectrum [8] , $R(\lambda)$ = spectral reflectance of the film

In an equivalent way we calculated the solar transmittance and the solar absorption (A_{Sol})

$$T_{Sol} = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda)W(\lambda)\partial\lambda}{\int_{\lambda_1}^{\lambda_2} W(\lambda)\partial\lambda}$$

$$A_{Sol} = 1 - (R_{Sol} + T_{Sol})$$

Applying the same calculation in the atmospheric window is a more complex issue, since the sky spectrum (atmospheric window range) is highly dependent on the humidity of the atmosphere. For simplicity we use atmospheric spectrum for clear sky as reported by Berdahl *et.al* [9] and in the same way $R_{8\text{-}13}$, $A_{8\text{-}13}$ and $T_{8\text{-}13}$ were calculated in the atmospheric window range. Table I gives the above optical functions values for all the samples reported in this work.

Figure 3 shows the FTIR spectra of polyethylene (A) and polyethylene with a film of Te (B) deposited as described above. The thickness of the Te layer was calculated as 0.12 μm based on the weight change of the polyethylene before and after Te deposition. The Mn-O treatment forms a brown, transparent film, which does not affect the FTIR spectrum to any noticeable extent, i.e., the Mn-O film is completely transparent in the entire IR region studied here. $KMnO_4$ pretreatment of the polyethylene was previously used as part of a series of treatments to improve adhesion of chemically deposited metal chalcogenide films to various polymer substrates [6]. In that work, the (supposedly MnO_2) film was removed chemically prior to further activation. In our case, we found that adhesion, and also homogeneity, of the subsequently deposited Te film was enhanced if the Mn-O film was not removed. Since this film did not detract in any way from the required properties of the Te film (in particular, good transparency in the mid IR), there was no reason to remove it. While we do not know the reason for this enhancement in adhesion (and therefore also homogeneity), it is possible that there is some degree of bonding between the O (or hydroxyl) of the Mn-O species and the polyethylene surface. While the polyethylene is essentially hydrophobic, even a low degree of hydrophilicity will allow better bonding with an O (OH) linkage compared with Te. Once the adherent Mn-O film has formed, the surface should then be more reactive to adsorption of other species (in this case, Te).

The average transmission of the Te film over the 8 - 13 μm window region (fig. 3b) is ca. 65% ($R_{8\text{-}13}$=0.652), compared to ca. 85% ($R_{8\text{-}13}$=0.813) for the bare (or Mn-O coated) polyethylene. The transmission of the Te film at 2.5 μm (which is close to the long wavelength edge of the solar spectrum) has dropped to 8%. It should be noted that the important parameter if the film is to be used as a solar shield is the total (direct + scattered) transmission. This is because the purpose of such a shield is to prevent solar radiation - whether direct or scattered - from reaching the cooling device located in the box. We were only able to measure the direct transmission in the mid IR range. However, the scattered transmission is clearly not very large, since the direct transmission is already quite high. In any case, consideration of scattered transmission would further increase the transmission. Therefore our measurements give a lower limit of this transmission.

Figure 4 shows the visible/near IR transmission spectra of the bare polyethylene (A), the Mn-O coated polyethylene (B) and of the Te film (C). Contrary to the FTIR measurements, total transmission is measured using the integrating sphere. For the visible/near IR region, any scattered component may be much more important than for the mid IR region. The reason for this is that, unlike the latter region, where transmission is high and a small increase in transmission will only have a small effect, the transmission in the visible/near IR region is very

low, and therefore even a small amount of additional transmission from scattered radiation could have a large effect (even a few percent of transmission in the solar region would be very deleterious for a cooling device).

The brown Mn-O film is much less transmitting (as expected) than the bare polyethylene in the visible region of the solar spectrum, an advantage for blocking the solar spectrum. The transmission of the Te film is shown on an expanded transmission scale in fig. 4(C). The integrated solar transmittance, T_{sol}, = 0.047.

While the transmission is the most important parameter for use as a solar shield, the reflectance is also important. This is because radiation which is not transmitted is either reflected or absorbed. Since absorbed radiation will cause heating of the shield, and therefore a certain degree of heating of the device (the extent depending on the geometry of the device and the heat flow characteristics of the surrounding ambient), the ideal shield should reflect all the solar radiation (up to 2.5 μm) but transmit the mid IR (8-12 μm).

Figure 5 shows the total (specular + diffuse) reflectance of the bare polyethylene (A), Mn-O coated polyethylene (B) and Te film (C). The Mn-O film considerably increases the reflectivity of the polyethylene over the visible region. The reflectance of the Te averages ca. 12% (R_{sol}=0.123) over the complete spectral range. The Te films prepared by this method exhibited good characteristics for use as solar radiation shields in radiative cooling devices. The mid IR transmission is good and excellent blocking in the solar spectral region is obtained. Further improvement could be made if the reflectivity of the film in the solar region was increased. However, a possibly simpler option to increase reflectivity of the shield would be to use a highly scattering, mid IR transmitting film on top of the Te. This could be, e.g., ZnS either deposited as a scattering film, or incorporated into the polyethylene with the Te underneath.

Applications of electrochemically-generated H_2Te: size-quantized semiconductor nanocrystals.

While the emphasis in this paper has been on the formation of Te films, the ease of preparation of H_2Te suggests other applications. The formation of nanocrystalline metal tellurides is an obvious one. While sulfides and selenides have been often prepared in the nanocrystalline form (typically ca. 5 nm crystal size) by simple precipitation from solutions of metal cations and hydrogen sulfide or selenide, tellurides have been much less studied, largely due to the difficulty in obtaining the unstable H_2Te. Since the interest in these nanocrystalline forms is often due to the quantum size effects shown by them (increase in bandgap - refs. 10 and 11 give short overviews of the main aspects of this field), tellurides, which usually exhibit larger quantum size effects than the corresponding sulfides or selenides, should naturally be of particular interest. We have observed that if H_2Te is passed through an ice-cooled alkaline solution of $CdSO_4$ complexed with nitriloacetate (the solution we use for chemical solution deposition of CdSe films which exhibit quantum size effects [11]), the initially colorless solution turns red, eventually precipitating a dark-red solid. Such a color is expected from CdTe with a crystal size between 4 and 5 nm [12]. Importantly, the dark-red precipitate turns black within minutes at room temperature, a clear sign of nanocrystal growth and therefore reduction of the optical bandgap toward the bulk value of 1.5 eV. Absorption spectroscopy of the red solution showed an absorption edge corresponding to ca. 2 eV.

Potential extension to electrochemical generation of H_2Se.

We did not succeed in using the electrochemical generation technique to form H_2Se since the conductivity of Se is much lower than that of Te and appreciable current cannot be passed

through a bulk Se electrode. It may be possible, using a composite electrode, such as mixed, finely divided Se and carbon, and preferably under illumination (Se is photoconductive) to extend this technique to generate H_2Se, which, although much more stable than H_2Te, is still relatively unstable. Both safety and cost considerations would justify such a method for H_2Se generation.

Conclusions

In this work we have described a method for the preparation of large area thin layers of tellurium on polyethylene foils using room-temperature decomposition of electrochemically generated hydrogen telluride. The tellurium layers exhibit high transmission in the mid-IR and are highly blocking in the solar spectral region. These characteristics are suitable for use as solar radiation shields in a radiative cooling device. Higher solar reflectivity would improve the layers even further for this application, and should be attainable by control of deposit morphology. The in situ preparation of H_2Te was also used to prepare CdTe nanocrystals exhibiting quantum size effects.

Acknowledgements. This work was supported under grant no. C13-219, Program in Science and Technology Cooperation, Economic Growth, U.S. Agency for International Development and by the European Programme Avicenne (No. AVI-CT94-0008).

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Figure captions

Fig. 1. XRD spectrum of: A) hexagonal Te deposit on the Mn-O/polyethylene B) bare polyethylene.

Fig. 2. SEM image of : A) Mn-O coated polyethylene B) Te deposit on the Mn-O/polyethylene.

Fig. 3. FTIR transmission spectra of bare polyethylene (A) and polyethylene with a ca. 0.12 μm film of Te (B).

Fig. 4. Visible/near IR total (direct + scattered) transmission spectra of polyethylene (A), Mn-O coated polyethylene (B), Te film on Mn-O coated polyethylene (C). Note the different scale for the Te film.

Fig. 5. Total (specular + diffuse) reflectance of the samples in fig. 4.

Table I. Optical functions values, R_{8-13}, A_{8-13} , T_{8-13} , R_{sol} T_{sol} and A_{sol} as defined in the text.

Table I.

Sample	T_{8-13}	R_{8-13}	A_{8-13}	T_{sol}	R_{sol}	A_{sol}
Polyethylene	0.81	0.156	0.03	0.89	0.07	0.03
Mn-O coat polyethylene.	0.80	0.170	0.02	0.72	0.17	0.10
Te Film.	0.65	0.221	0.13	0.04	0.12	0.83

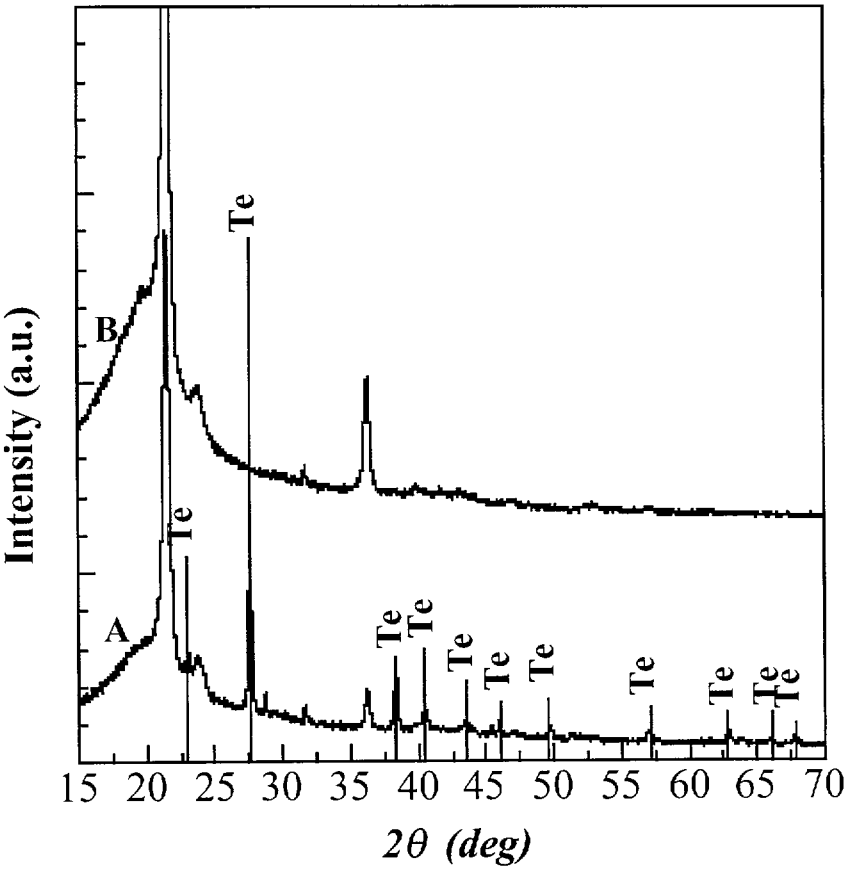

Intensity (a.u.)
B
A
Te
Te
Te
Te
Te
Te
Te
Te
Te
Te
Te
15 20 25 30 35 40 45 50 55 60 65 70
2θ (deg)

Fig. 1

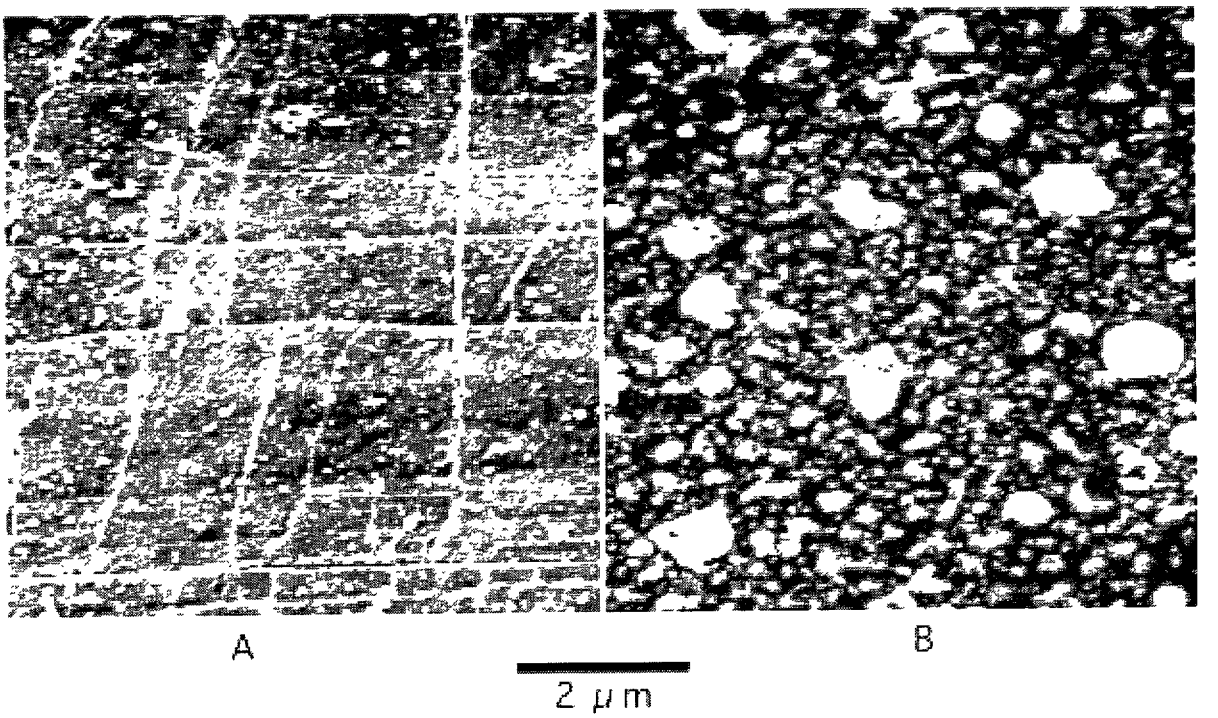
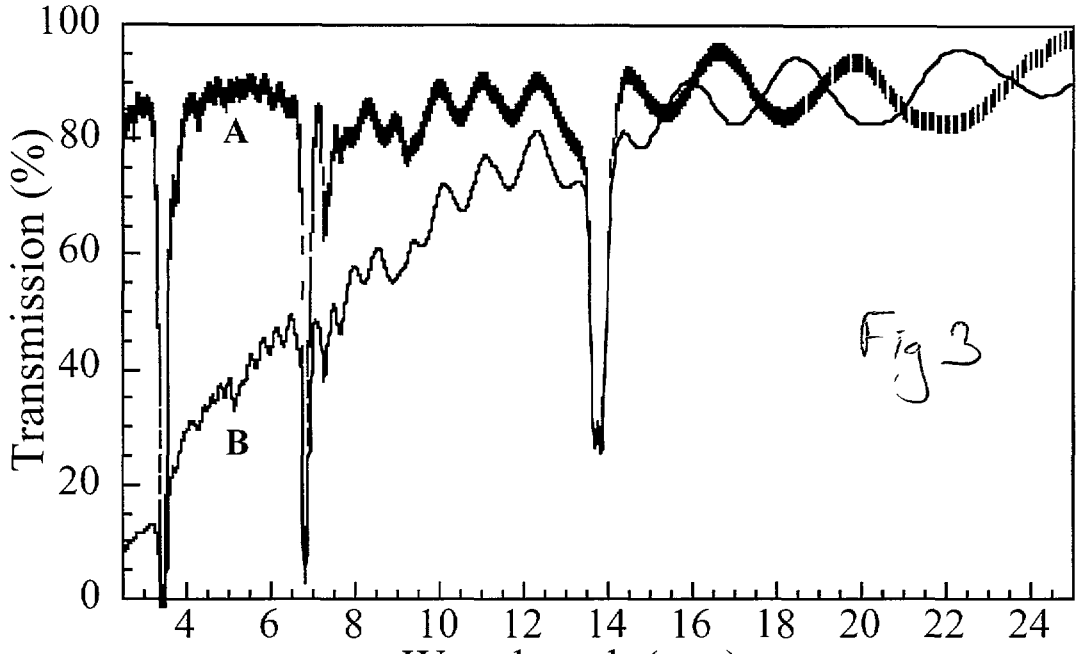
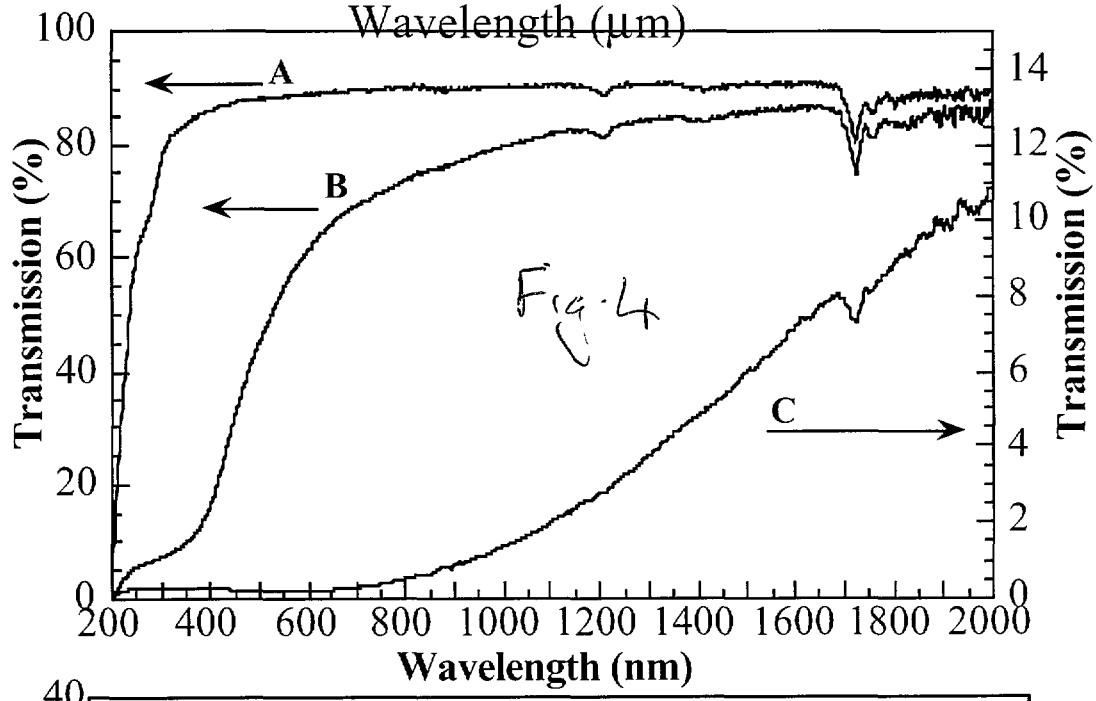
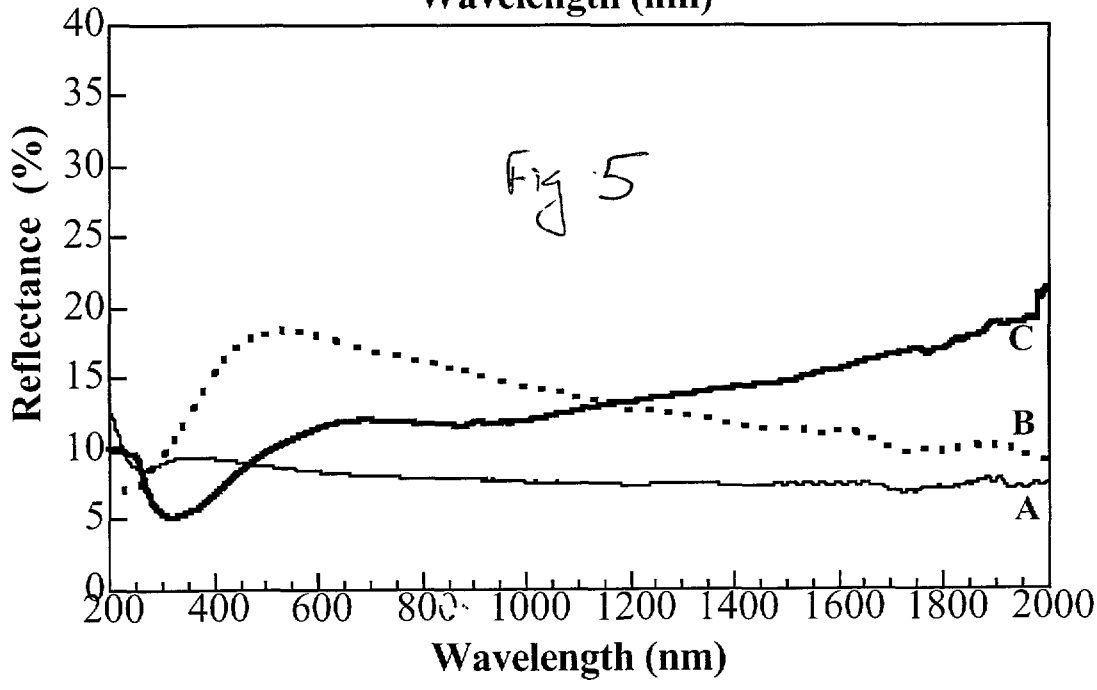

A
B
2 μm

Fig. 2


Transmission (%)
Wavelength (μm)
A
B
Fig 3


Transmission (%)
Transmission (%)
Wavelength (nm)
A
B
C
Fig. 4


Reflectance (%)
Wavelength (nm)
A
B
C
Fig 5