ORIGINAL PAPER

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Adsorption of O_2 and $HF(O_2)$ on Thermally Evaporated Tellurium Films

Abstract: The room temperature variation of surface conductance of tellurium (Te) films with thickness has been studied. The measurements were performed in an atmosphere of oxygen (O_2) or oxygen bubbled through hydrofluoric acid ($HF(O_2)$). Tellurium films of thicknesses 500, 1000, 1500 and 2000A were deposited by thermal evaporation at a vacuum maintained at about 10-5 torr during the evaporation process. Some of the Te samples were annealed at 200°C for 20 minutes. For the current (I) – voltage (V) measurements, the two-point probe configuration was adopted using aluminium (Al) electrodes. The surface conductance at zero bias was determined from the I – V data.

The results reveal that the surface conductance of Te films is enhanced by the adsorpion of O_2. while the adsorption of $HF(O_2)$ reduces the surface conductance of the samples. The evaluated increase in surface conductance at zero bias, due to the adsorption of O_2 ranges from 92% to 113% as the thickness of the films varied from 500 to 2000A. Also, the value of the reduction in surface conductance due to the adsorption of $HF(O_2)$ is between 27% and 33% as the thickness of the films varied from 500 to 2000A. the surface conductance of all the samples investigated increases exponentially with thickness. Fimally, the surface conductance of as-deposited Te films is higher than that of heat-treated Te samples.

Key words: Condensed matter - Electical Properties of thin films - Surface Statuse

إدمصاص الأوكسجين و حامض الهيدروفلوريك بواسطة التبخير الحراري على أفلام التيلوريوم (Te)

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المستخلص :لقد درست التغيرات في التوصيل السطحي لمادة التيلوريوم (Te) بسماكات مختلفة على درجة حرارة الحجرة . وقد أجريت التجارب في وجود جو من الأوكسجين (O_2) أو عن طريق إدخال الأوكسجين على شكل فقاعات من خلال حامض الهيدروفلوريك . (HF(O2)) وقد تم تحضير أغشية التيلوريوم بسماكات 500 ، 1000 ، 2000 أيتروم بواسطة التبخير الحراري في وجود تفريغ مقداره (10 تور) خلال عملية التبخير . بعض عينان التيلوريوم تم تحضيرها بالتعريض إلى درجة حرارة 200 م لمدة 20 دقيقة . وقد أخذت القياسات عند تيار مقداره (I) وشده تيار مقداره (V) ، وذلك بإعتماد طريقة المحسب ذو الطرفين وإستخدام الألمنيوم (AL) كموصل كهربائي . لقد تم إعتماد التوصيل السطحي على نقطة صفر بين للنتائج من . V - I. تظهر النتائج بأن التوصيل السطحي لأغشية التيلوريوم (Te) قد تحسن في وجود الأوكسجين (O_2) ، ولكن إستخدام حامض الهيدروفلوريك ($HF(O_2)$) قد قلل التوصيل السطحي للعينات المدروسة . إن قياس الزيادة في التوصيل السطحي على نقطة صفر بين ، قد تم في وجود جو من الأوكسجين بتراوح ما بين 500 – 2000 آيتروم . وكذلك الحال فإن النقص في التوصيل السطحي قد تم حسابه عند إستخدام حامض الهيدروفلوريك ($HF(O_2)$) بتركيز يتراوح ما بين 27% – 33% ، وعندما كان سمك الغشاء بتراوح ما بين 500 – 2000 آيتروم . إن التوصيل السطحي لجميع العينات المدروسة قد زاد بطريقة تصاعدية مع زيادة سمك الغشاء . وأخيراً فإن التوصيل السطحي لأغشية التيلورويوم (Te) المرسبة بالطريقة الطبيعية كان أعلى من تلك الأغشية المحضرة بإستخدام المعاملة الحرارية .

كلمات مدخلية: المواد المكثفة – الخواص الالكترونية للأفلام الرقيقة – خواص السطوح

Introduction

Tellurium is one of the most studied materials among the elemental semiconductors because of its application in devices such as thin film transistors (Keller and Stuke 1965, Okuyama, Yamashita, Chiba and Kumagai 1977 and Solymar and Walsh 1991) and strain sensor (Rideout 1978). Also, several investigations (Chaudhuri 1974, Okuyama *et al.* 1975, Phahle 1977, Saha 1981, Bar-Lev 1993, Askeland 1994, Oberafo *et al* 1994 and Mukolu 1997) have been carried out on tellurium partly due to its technological potentials and because it can be evaporated easily without the problem of dissociation (Phahle 1977). Oxygen is one of the natural contaminants to which most semiconductor surfaces are exposed at some stage during device preparation and operation. Therefore, since the reliability and stability of most devices made from tellurium are intimately related to their surface

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conditions, investigating the effect of O_2 on the surface conductance of Te, will be of great importance to device operations.

It has been reported that most etchants of tellurium contain hydrofluoric acid (HF) as one of their components (Krupanidhi 1983). Thus, dry, post-etching HF residue on the Te surface could together with the O_2 of the air have some influence on the surface-dependent properties of Te. Hence, the present work also aims at investigating the combined effect of O_2 and HF on the surface conductance of Te by allowing O_2 through aqueous HF, ($HF(O_2)$) to interact with the evaporated Te surface.

It is well established that the electrical properties of thin films are strongly influenced by film structure (Chaudhuri 1974). Therefore, one of the most important prerequisites for a fundamental understanding of the ambient effect on Te surface is a knowledge of its structure. It has been reported that thermally evaporated tellurium films show p-type conductivity because of the presence of lattice defects which act as acceptors (Phahle 1977).

The present work is to investigate the effects of O_2 and $HF(O_2)$ on evaporated tellurium films of various thicknesses using aluminium electrode contacts. The current-voltage measurements would be taken in vacuum, and in O_2 and $HF(O_2)$ ambients at room temperature.

From the I – V data, the surface conductance would be determined.

Experimental Procedure

- **Sample Fabrication.**

Tellurium films of thicknesses 500, 1000, 1500 and 2000A were deposited by thermal evaporation from a tungsten filament in a chamber maintained at a vacuum of about 10^{-5} torr using an Edwards, model 306 coater. The deposition rate, which was about 500A min^{-1}, was determined with an Edwards, model 306 Film Thickness Monitor.

Some of the Te samples were annealed at 200°C for 20 minutes. Thereafter, Al contact electrodes were deposited on the surfaces of the annealed and the unannealed Te films by using the same process of deposition. All the electrodes were 500A thick. The samples were prepared from appropriate quantities of elemental tellurium and aluminium, each of 99.999% purity (Ventron, Germany). The dimensions and configurations of the samples used for the I – V measurements are shown in Figure 1.

The samples were in two configurations, namely high field and low field. For the high field samples, the inter-electrode distance was 2mm, while for the low field samples, the separation was 20mm.

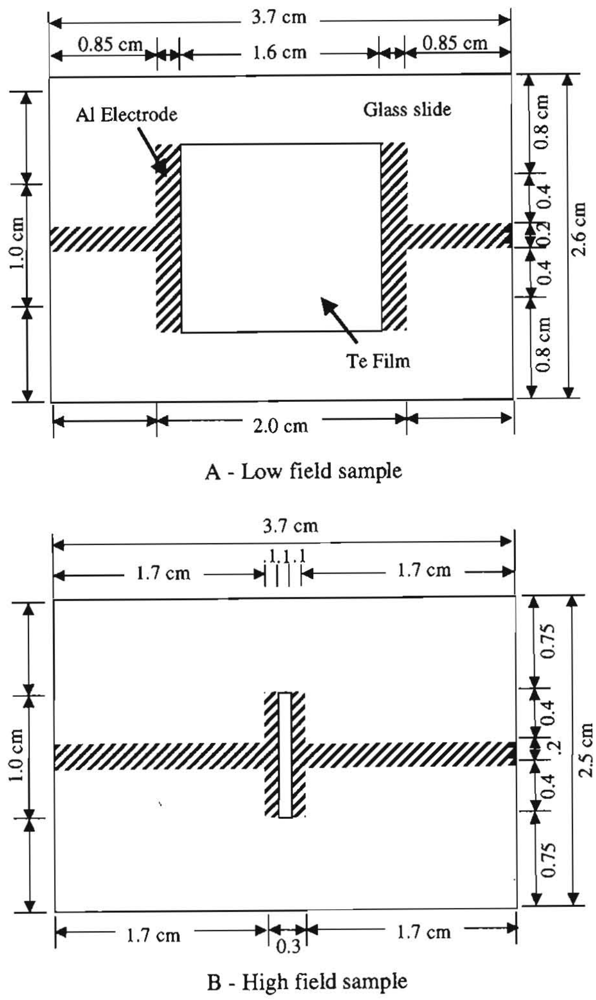
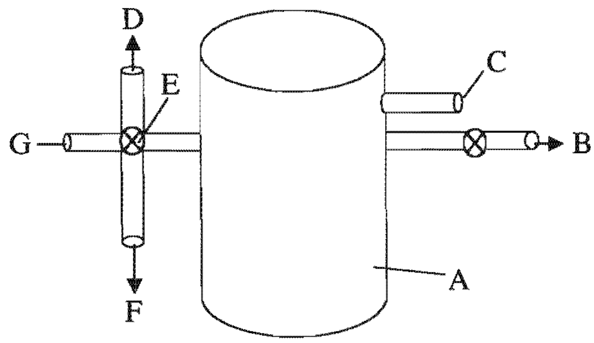


Fig. 1 Dimensions and configurations of the samples used for the I-V measurements in cms.

- **Adsorption of Oxygen**

The arrangement of the apparatus for the study of adsorption of oxygen on Te is shown in Figure 2. The adsorption vessel was made of brass and was connected via a manometer to a storage cylinder containing the purified oxygen required for the experiment. There is also a port for connection to a vacuum pump.

After the sample under investigation was put in the adsorption vessel, oxygen was admitted at a pressure of 780mm Hg and monitored continuously on the manometer. After about 30 minutes, and with the oxygen flow still maintained, current-voltage data were taken. The current was measured with a Keithley 160B digital electrometer, while the voltage was measured with a digital millivoltmeter (Hewlett-Packard type 3465A). All the measurements were taken at room temperature.

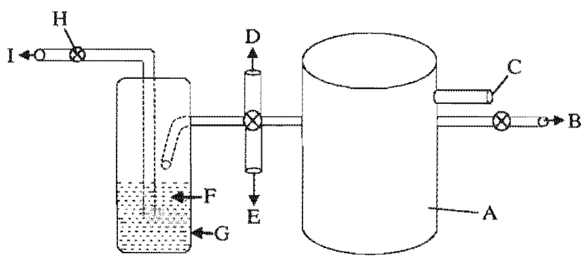


A Adsorption vessel
B Outlet
C Connecting outlets from ammeter, voltmeter and thermocouple to the test sample
D To manometer
E Tap
F To vacuum pump
G To oxygen cylinder

Fig. 2 Apparatus used for the investigation of adsorption of O_2

- **Adsorption of HF(O_2)**

The experimental set up was the same as the one described earlier for the adsorption of O_2 except that a vessel containing hydrofluoric acid (HF) was introduced between the oxygen cylinder and the adsorption vessel as shown in Figure 3. The vessel of HF is made of polytetrafluoroethene (teflon) since it is resistant to the attack of HF. Oxygen, maintained at a pressure of 770mm Hg, was bubbled through the HF into the adsorption vessel containing the test sample, the HF was of 99.99% purity (Ventron, Germany). By varying the voltage from 0 to 100V, the currents were measured with a digital electrometer (Keithley type 160B) . All the measurements were carried out at room temperature.



A Adsorption vessel
B Outlet
C Connecting outlets from ammeter, voltmeter and thermocouple to the test sample
D To manometer
E To vacuum pump
F Hydrofluoric acid
G Teflon flask
H Tap
G To oxygen cylinder

Fig. 3 Experiment set up for the adsorption of HF O_2

- **Verification of the Carrier Type of the Thermally Evaporated Tellurium Films by the Hot Probe Method.**

The surface of each sample was touched by two identical metal probes between which a galvanometer was connected. One of the probes was heated while the other was at room temperature. Thereafter, the galvanometer was observed for the direction of current flow which determined the type of carrier.

Results

The results of the variation of surface conductance with thickness for Al-Te-Al samples in vacuum, 0_2 and HF (0_2) ambients at 300K are shown in Figures 4 and 5. These figures show that the surface conductance of Al-Te-Al samples increases exponentially as the thickness of the film increases.

Also, the values of surface conductance of Al-Te-Al samples in vacuum, 0_2 and HF (0_2) ambients are presented in Table 1. These results reveal that the surface conductance of the samples is enhanced by the adsorption of 0_2 while the adsorption of HF (0_2) reduces the surface conductance of the samples.

Discussion

- **Effect of Oxygen on the Surface Conductance of Al-Te-Al samples**

The present experimental results reveal that oxygen increases the surface conductance of thermally evaporated tellurium films. This is achieved by a band bending effect due to oxygen adsorbed on the surface of tellurium which causes small changes in the density of states at the Fermi level. Since oxygen has a strong electron affinity, it would induce acceptor states (Many 1959). The acceptor states are then filled with electrons excited from the valence band, thus leaving an equal number of holes behind in the valence band. This leads to a pronounced band bending downward near the surface of the Te film. If a field is applied along the surface of tellurium, the holes would move and thus give rise to an electric current which increases its surface conductance as observed in the present investigation. From Table 1, the increase in surface conductance at zero bias is between 3.40×10^{-3} and 3.90×10^{-2} $\Omega^{-1}cm^{-2}$ for Al-Te-Al samples.

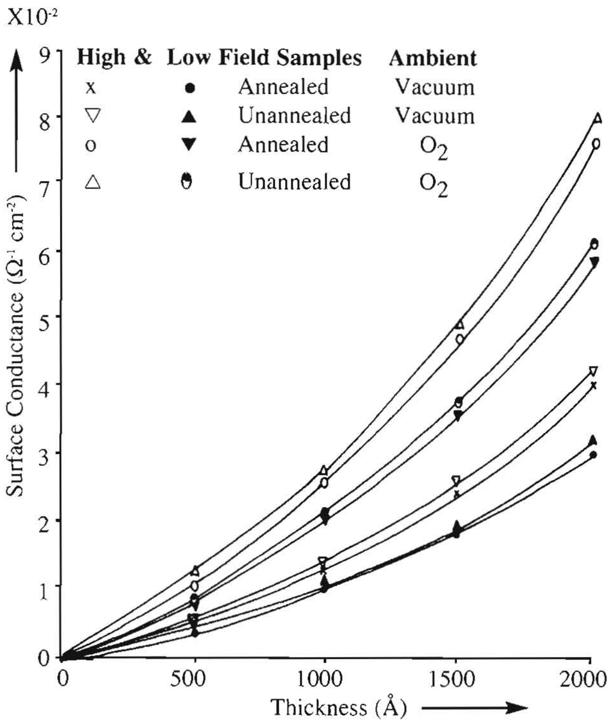


Fig. 4 Variation of surface conductance with thickness for A1-Te-A1 samples in vacuum and O_2 ambient at 300k

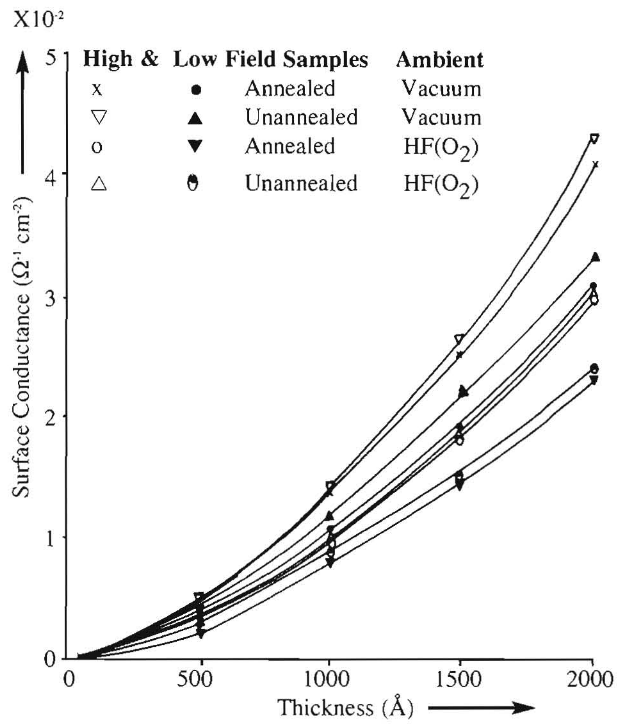


Fig. 5 Variation of surface conductance with thickness for A1-Te-A1 samples in vacuum and $HF(O_2)$ ambient at 300k

Table 1. Surface Conductance of Al-Te-Al samples in vacuum, O_2 and $HF(O_2)$ ambients

Nature of sample	Ambient	Surface conductance at different thicknesses (Ω^{-1} cm^{-2}) X 10^{-2}			
		500 Å	1000 Å	1500 Å	2000 Å
Annealed/Low field	Vacuum	0.3	0.8	1.6	2.9
Unannealed/Low field	Vacuum	0.4	0.9	1.7	3.2
Annealed/High field	Vacuum	0.5	1.1	2.4	4.0
Unannealed/High field	Vacuum	0.6	1.2	2.6	4.2
Annealed/Low field	O_2	0.7	1.9	3.8	5.8
Unannealed/Low field	O_2	0.8	2.0	3.9	6.0
Annealed/High field	O_2	0.9	2.7	4.7	7.5
Unannealed/High field	O_2	1.2	2.9	5.0	8.1
Annealed/Low field	$Hf(O_2)$	0.2	0.7	1.3	2.0
Unannealed/Low field	$Hf(O_2)$	0.3	0.8	1.4	2.3
Annealed/High field	$Hf(O_2)$	0.4	0.9	1.7	2.9
Unannealed/High field	$Hf(O_2)$	0.5	1.0	1.8	3.1

- **Effect of $HF(O_2)$ on the Surface Conductance of Thermally Evaporated Tellurium Films.**

From the results illustrated in Figure 5, it is evident that hydrofluoric acid oxidation ($HF(O_2)$) reduces the surface conductance of Al-Te-Al samples. For explanation, we note that amorphous semiconductors are known (Spear *et al* 1974) to have a large density of states in the mobility gap which originate from dangling bonds or defects inherent in the material. Also, it has been reported by Du, Salkalachen, Yao, Froelich, John and Tong (1989) that the presence of hydrogen in silicon can terminate the dangling bonds and consequently reduce the density of states in the band gap. Therefore, it is expected that the bubbling of oxygen through hydrofluoric acid at room temperature results in the elimination of defects on the tellurium surface since hydrofluoric acid contains hydrogen. The removal of defects decreases the dangling bond density, presumably due to a coalescence of voids. The coalescence would be achieved by the combination of $HF(O_2)$ with the dangling bonds. Since the carrier concentration at the surface of tellurium decreases concomitantly, the surface conductance should decrease as observed in the present measurement. The observed value of the reduction in surface conductance at zero bias, is between 1.00×10^{-3} and $1.15 \times 10^{-2} \Omega^{-1} cm^{-2}$ for Al-Te-Al samples.

- **Effect of Heat Treatment**

From the present measurement, it was observed that the surface conductance of as-deposited Te films is higher than that of heat-treated Te samples. Annealing is known to eliminate defects due to coagulation of voids (Mott and Davis 1979). The elimination of defects decreases the dangling bond density with a corresponding decrease in carrier concentration. As a result of this the surface conductance of Te decreases on annealing. However, the results obtained indicate that the annealing time of 20 minutes is effective in improving the electronic properties of the tellurium films.

During the verification of the carrier type of the thermally evaporated tellurium films by the hot probe method, the hot probe heats the films immediately under it, with a consequent rise in the kinetic energy of the free carriers there. These then move with higher velocities than their cooler neighbours. Therefore, the majority carriers at the hot probe diffuse out to the cold probe. This results in the hot region becoming slightly depleted of majority carriers and acquiring the potential of the ionized impurities there while the vicinity of the cold probe remains neutral; current flows in the galvanometer, the direction of which depends on the sign of the charge of the ionized impurity. Since the hot probe was more negative with respect to the cold probe, it shows that the sample investigated behaves like a p-type semiconductor.

Conclusions

The following conclusions can be made from the present study:

(1) The adsorption of O_2 on evaporated tellurium surface at a pressure of 780mm Hg raises its surface conductance. The increase in surface conductance at zero bias is between 3.4×10^{-3} and $3.9 \times 10^{-2} \Omega^{-1} cm^{-2}$ as the thickness of the films increased from 500 to 2000A.

(2) The adsorption of $HF(O_2)$ at a pressure of 770mm Hg reduces the surface conductance of Al-Te-Al samples. The observed value of the reduction in surface conductance at zero bias is between 1.00×10^{-3} and $1.15 \times 10^{-2} \Omega^{-1} cm^{-2}$ as the thickness of the films varied from 500 to 2000A.

(3) The surface conductance of as-deposited Te films is higher than that of heat-treated Te samples.

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