Effects of Cu Diffusion from ZnTe:Cu/Ti Contacts on Carrier Lifetime of CdS/CdTe Thin Film Solar Cells

Preprint

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EFFECTS OF Cu DIFFUSION FROM ZnTe:Cu/Ti CONTACTS
ON CARRIER LIFETIME OF CdS/CdTe THIN FILM SOLAR CELLS

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ABSTRACT

We study the performance of CdS/CdTe thin film PV devices processed with a ZnTe:Cu/Ti contact to investigate how carrier lifetime (τ) in the CdTe layer is affected by Cu diffusion from the contact. Time-resolved photoluminescence (TRPL) measurements show that τ decreases slightly as the contacting temperature increases in the temperature regime that produces "insufficient" Cu concentration in CdTe (~room temperature to ~250° C). However, τ increases significantly once the contact temperature is in the range that yields "optimum" Cu concentration and high-performance devices (~280 to ~320ºC). At higher substrate temperatures (>~300° C), τ drops precipitously, consistent with a region previously identified as producing "excessive" Cu concentration - and poor device performance. The observed τ increase within the "optimum temperature" range not only suggests why high-performance devices may form at these contact temperatures using many different contact processes (including paste contacts), but may provide a significant clue as to why Cu-contact formation processes impart a broad latitude in other process parameters.

INTRODUCTION

It is well known that controlled Cu diffusion from the back contact of a CdS/CdTe thin film solar cell can significantly enhance device performance. It is also well known that this same Cu diffusion is often linked to device instability. Although some Cu-free contact designs have produced devices that demonstrate high stability, these contacts have not yet achieved performance consistent with devices that incorporate Cu-containing contacts. This suggests that the CdTe photovoltaic (PV) community presently lacks clear understanding of the role(s) of Cu in junction formation, and a prudent research strategy should continue to advance this understanding. Research at NREL using the ZnTe:Cu/Ti contact has enabled critical aspects of Cu diffusion to be studied using conditions that afford a high degree of process control. Some of the insight gained from these studies is described below.

We have established that Cu diffusion from the ZnTe:Cu layer can increase the net acceptor concentration in the CdTe layer (N_a-N_d), thereby reducing the space-charge width (W_d) of the junction. Optimum light current-voltage (LIV) performance is attained when W_d is narrow enough to produce a drift field in the CdTe absorber of sufficient strength to overcome the relatively poor carrier lifetime, τ, but still wide enough to limit effects of voltage-dependent collection (i.e., photocarriers should be generated primarily within of the depletion region when the device is biased near the maximum power point [MPP]) [1]. An "optimum contact" is produced by "optimum Cu diffusion" resulting in a W_d of ~0.3 to 0.5 µm when the device is biased near MPP. If Cu incorporation from the contact increases beyond its optimum concentration, N_a-N_d can continue to increase, and lower values of reverse saturation current (J_o) can result. Unfortunately, this amount of Cu incorporation will produce voltage-dependent collection because the W_d is too narrow. Cu can also diffuse into the CdS layer, reduce this layer's net donor density (N_d-N_a), and produce a manifestation of photoconductivity, as confirmed by red vs. blue light-bias voltage-dependent quantum efficiency [2]. These complications moderate the potential benefits of a lower J_o, reducing the open-circuit voltage (V_{oc}) and fill factor of the device. Similar (but longer-term) redistribution of Cu into the CdS layer may be linked to certain types of device instability.

In the above description, a tacit assumption is that τ in the CdTe layer is not significantly affected as Cu concentration in the CdTe increases. In this study, we have tested this assumption using time-resolved photoluminescence (TRPL) measurements of sets of well-characterized ZnTe:Cu/Ti-contacted devices.

EXPERIMENTAL

CdS/CdTe materials used in this study were produced by three different groups. The samples produced at NREL incorporated 7059 Glass, SnO_2:F/SnO_2 produced by chemical vapor deposition from $CBrF_3$, $Sn(CH_3)_4$, and O_2 CdS deposited by solution growth, CdTe deposited by CSS, and a vapor $CdCl_2$ process [3]. The second sample set was produced at Colorado State University (CSU) and utilized Tec 15 (soda lime) glass substrates, with CdS, CdTe, and $CdCl_2$ processed in vacuum using the CSU reactor [4]. The third set of samples was produced using Tec 15 glass, a commercial vapor transport deposition (VTD) process, for CdS and CdTe, and a wet $CdCl_2$ process. For all CdS/CdTe materials, no contact or precontact process was performed prior to the application of the ZnTe:Cu/Ti contact.

The ZnTe:Cu/Ti contact was produced at NREL as follows: Samples were placed into a multisource vacuum processing chamber and preheated for 120 min at the indicated contact deposition temperature (25 to 360°C). Prior to ZnTe:Cu deposition, ion-beam milling was performed with a 3-cm Kaufman-type ion gun, operating at

1

a beam energy and current of 500 eV and 6 mA, respectively, using UHP-grade Ar. ZnTe:Cu layers (~9 at.% Cu) were deposited by r.f. sputter deposition to the desired thicknesses (1.0 µm for the temperature study, and 0.04, 0.1, 0.2, 0.5, or 1.0 µm for the thickness study). The sample heater was turned off following ZnTe:Cu deposition and allowed to cool to an indicated temperature of ~185°C (unnecessary for 25°C sample), at which point 0.5 µm of Ti was deposited using d.c. magnetron sputtering. Following contact formation, a pattern of individual 0.25-cm^2 cells were defined photolithographically on each sample. Cell definition was by two-step chemical etching, first using TFT Ti Etchant (Transene Co. Inc., Rowley, MA) to remove the Ti, followed by an aqueous solution of 39% FeCl$_3$ to remove the ZnTe:Cu and CdTe. A perimeter contact to the SnO$_2$ layer was formed with ultrasonically soldered In.

Electrical analysis included light and dark current-voltage (LIV/DIV) measurements at room temperature using an XT-10 solar simulator adjusted to approximate Global AM1.5 current from a CdS/CdTe reference cell. Capacitance-voltage (C-V) measurements were performed in the dark using an HP 4274 LCR meter at a frequency of 100 kHz within a bias voltage range of –2.0 to +0.6 volts (i.e., forward bias to the approximate MPP voltage of the devices).

Secondary ion mass spectrometry (SIMS) analysis was performed on some devices following chemical removal of the Ti layer with the TFT etchant. SIMS was performed from the contacted side of the devices using a Cameca IMS-3F instrument tuned for a mass resolution (M/ΔM) of ~4000 to allow for separation of $^{63}Cu^+$ from $^{126}Te^{2+}$ species.

TRPL was measured at 820 nm through the glass side of the devices using a 650-nm excitation wavelength and a beam diameter of ~1 mm at a 250 kHz rep rate. Measurements were performed at two different laser-injection intensities (0.25 and 2.5 mW average CW power) in the hope of observing and negating any effect that increasing electric field strength as a function of Cu incorporation may have on the measurement of τ.

RESULTS AND DISCUSSION

Previous studies have shown that the parameters of the ZnTe:Cu/Ti back contact that affect Cu diffusion also influence the electrical performance of the resultant device (see for example Figure 1). Diffusion-linked parameters include the temperature during contact processing and the amount of Cu available at the contact (as determined by the thickness of the ZnTe:Cu layer). Figures 2 and 3 show SIMS profiles confirming systematic variation in Cu diffusion due to contact temperature (Fig. 2) and Cu availability (Fig. 3). Figure 4 shows C-V analysis indicating that an increase in net acceptor concentration (N$_A$-N$_D$) is observed for changes in ZnTe:Cu thickness. These changes coincide with the increase in Cu concentration shown in Figures 3. A similar (but not shown) trend in the C-V data has also been established

showing that increasing contact temperature increases N$_A$-N$_D$ [5]. Numerical simulation has further linked the general trends in observed device performance with these changes in N$_A$-N$_D$ [1].
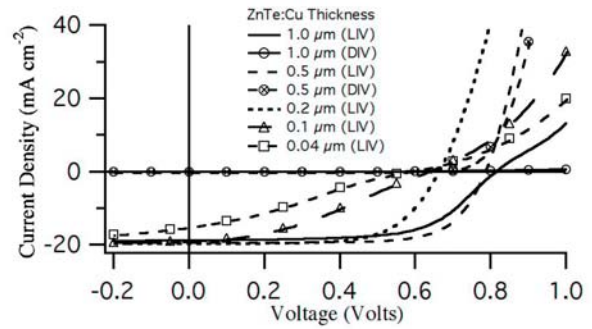

Fig. 1. IV characteristics for CdS/CdTe/ZnTe:Cu/Ti devices contacted at 360°C as a function of the indicated ZnTe:Cu thickness.
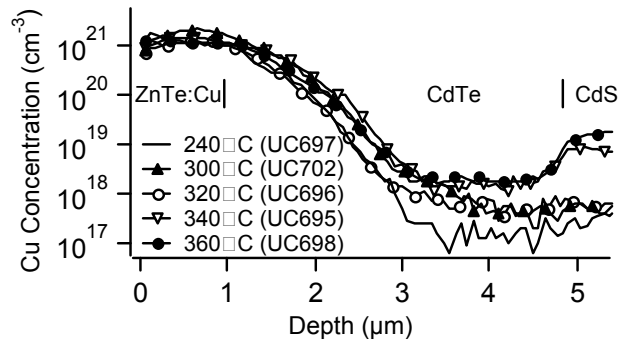

Fig. 2. Quantified SIMS depth profiles of Cu concentration in CdTe/CdS devices for indicated approximate contact temperature. Analysis was performed from the ZnTe side.
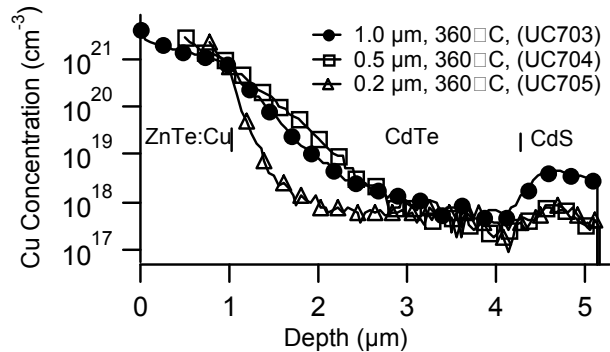

Fig. 3. Quantified SIMS depth profiles of Cu concentration in CdTe/CdS devices for indicated ZnTe:Cu thickness. Analysis was performed from the ZnTe side. The approximate ZnTe:Cu/CdTe is interface indicated as "0" depth.
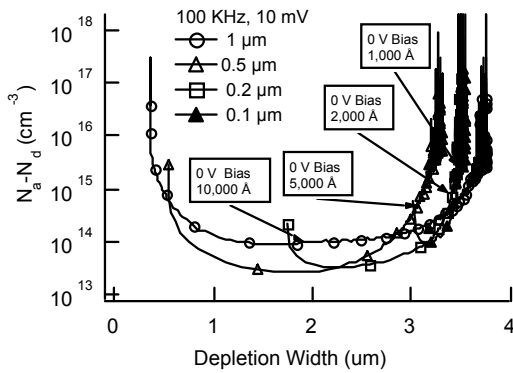
Fig. 4. C-V analysis (room temperature, dark) for devices with indicated ZnTe:Cu thickness. Maximum forward voltage is 0.6 V. Location of W_d is indicated for each data set at location of arrow.

The preceding review suggests a compelling description of junction evolution during Cu contact formation. However, it does not account for reports detailing reduction in τ with Cu incorporation [6,7,8]. If reduction in τ with increasing Cu is true for all Cu containing CdTe back contacts (including the ZnTe:Cu/Ti contact), it is difficult to describe why voltage-dependant collection *decreases* near optimum Cu incorporation [5]. Specifically, a shorter minority-carrier diffusion length (i.e., reduced τ) would make it increasingly difficult to collect carriers outside of an increasingly narrow depleted region. This study has been designed to examine how τ may evolve as Cu diffuses from the ZnTe:Cu/Ti contact. Because Cu incorporation into the CdTe layer is known to increase with both contact temperature and Cu availability for the ZnTe:Cu/Ti contact (shown in Figs. 2 and 3), two different studies were conducted. The first examines how τ varies as a function of contact deposition temperature (at near-optimum ZnTe:Cu thickness), while the second examines variation in τ with ZnTe:Cu layer thickness (at near-optimum contact temperature).

The sample sets used for the first TRPL study include those shown in Figs. 1-4. This set was produced using material from the commercial VTD process. Figure 5 shows the TRPL-measured lifetime as a function of ZnTe:Cu layer deposition temperature. Inspection of the related PL decay curves for individual cells show that these samples demonstrate a gentle biexponential decay at 2.5 mW. At lower intensity (0.25 mW), the fast decay component makes the biexponential aspect of the decay more pronounced. Longer duration scans taken at even lower intensity (~0.07 mW) for two samples indicated a continuing decrease in lifetime with decreasing injection level (note that signal intensity becomes borderline at this injection level). This injection dependence is in contrast to what is observed for cells measured at NREL with other types of contacts [6], and could be a sign of charge separation consistent with a stronger junction field in these devices relative to previously measured devices. However, trap recombination and saturation are also possible explanations.

Because the photoluminescence decay for these devices was biexponential, values of τ were calculated from biexponential fits for both the "fast" decay region (τ_1) and for the longer-term decay (τ_2). The different functional forms suggest that τ_1 at 0.25 mW may be more representative of interface recombination kinetics, whereas the other τ values are more representative of bulk recombination. τ values for both fast and slow regions are shown in Fig. 5. The results indicate that some of these samples demonstrate very respectable lifetimes for CdTe PV devices. This is especially true at the higher injection level (2.5 mW) where the influence of junction field should be screened efficiently by the photoinjected carriers.
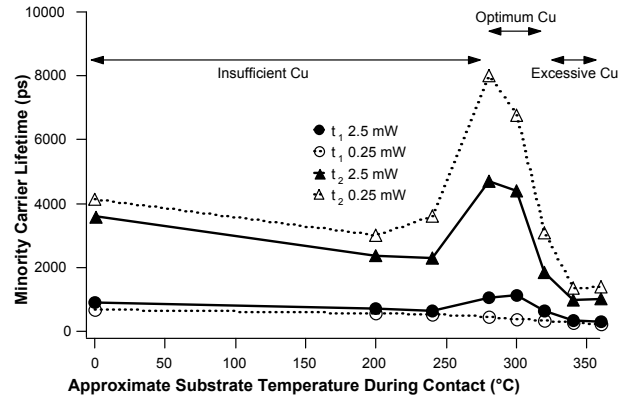

Fig. 5. Minority carrier lifetime in the junction region of a CdS/CdTe/ZnTe:Cu/Ti device as a function of contacting temperature. Figure shows two different excitation intensities (2.5 mW and 0.25 mW) and fits of the fast (t_1) and slow (t_2) decay times. The temperature regions indicated as "Insufficient Cu," Optimum Cu," and "Excessive Cu" are consistent with those identified in Figs. 2 and 3.

Trend analysis of τ with Cu diffusion (Fig. 5) shows that τ decreases slightly as the contacting temperature increases from room temperature to ~250°C. Previous studies have shown that this temperature region yields CdTe Cu concentrations that are considered "insufficient" for high-performance devices [1,5], The most exciting result of this study is observed in the contact temperature range of ~280 to ~320°C, where τ is observed to increase significantly. Previous studies have shown this temperature range produces a Cu concentration in the CdTe that is "optimum" for producing high-performance devices. Finally, the figure shows that for substrate temperatures >~300°C, τ drops precipitously, consistent with a region previously identified as producing "excessive" Cu concentration and poor device performance. The observed τ increase within the "optimum" temperature range not only suggests why high-performance devices result in that temperature range for the ZnTe:Cu/Ti contact, but may suggest why other contact processes tend to be optimized within this temperature range. The result may also suggest why the Cu-contact formation processes are often "forgiving" of

changes in the contact process parameters (i.e., a contact process may yield a W_d that is either too wide or too narrow, but still produce a good device because the longer τ will allow for enhanced collection in lower-field regions of the junction).

Upon initial inspection, the observation that τ can increase with Cu diffusion appears to be in stark contrast to existing reports that indicate τ decreases *monotonically* with increasing Cu diffusion into CdS/CdTe [6,7]. However, it should be noted that in those studies, Cu incorporation into the CdTe and CdS layers was varied by changing the amount of Cu available from the contact processes at near-optimum temperature (i.e., fixing the diffusion temperature at ~280°C and changing the Cu metal thickness). For the study shown in Fig. 5, the Cu diffusion was controlled by varying the contact temperature while maintaining a fixed amount of Cu available to the contact (i.e., the ZnTe:Cu thickness remained constant at ~5000 Å). Additionally, for most other contacts, the lowest amount of Cu that can be diffused into the CdTe is known to produce apparent quantum efficiency under red-light bias that exceeds 100% in the CdS-absorbing region [2]. In contrast, the extent of Cu diffusion during the ZnTe:Cu/Ti contacting can be controlled so that devices with optimum performance result, yet QE greater than expected from the CdS region does not result (i.e., Cu does not diffuse significantly into the CdS, see Figure 6). A final difference to consider is that Cu diffusion in the ZnTe:Cu contacting process occurs at a slightly higher temperature than is typical for Cu-based CdTe contacts (280-350°C, compared to ≤280°C). This higher-temperature diffusion may provide benefits similar to those observed during the ~400°C $CdCl_2$ process (i.e., many $CdCl_2$ sources contain Cu as a residual contaminant).
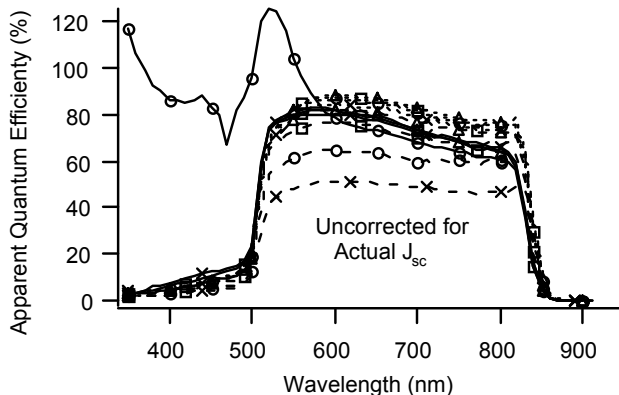

Fig. 6. Apparent quantum efficiency (AQE) analysis of ZnTe:Cu/Ti-contacted samples of Fig. 2 with "insufficient" (dashed lines), "optimum" (dotted lines), and "excessive" (solid lines) Cu at zero-volts bias and various light bias conditions (triangles = no light bias, crosses = white light, squares = blue light, and circles = red light). Notable changes in the AQE are only observed under red-light bias for the "excessive" Cu condition, indicating that sufficient

Cu has diffused into the CdS to cause apparent photoconductivity in this layer.

Considering the above results, an additional TRPL study was performed that more closely replicates the experimental design of previous Cu diffusion studies but using the ZnTe:Cu contact. This study fixed the temperature the ZnTe:Cu/Ti contact near an optimum value and varied the Cu diffusion by varying the ZnTe:Cu thickness. If the ZnTe:Cu/Ti contact behaved like contacts based on other Cu sources (e.g., Cu_xTe, metallic Cu, etc.), the expected observation would be a monotonic decrease in τ with ZnTe:Cu thickness. This study also included CdS/CdTe structures produced by several different groups to allow an investigation of how τ functionality may be affected by different materials.
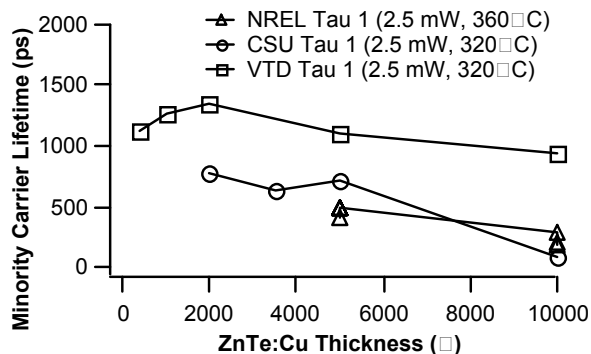

Fig. 7. TRPL analysis showing changes in τ_1 as a function of ZnTe:Cu thickness at indicated contact deposition temperature.

Unlike the results of the initial study (i.e., effect of contact temperature on τ), the results of the second study (Fig. 7) are much more consistent with previous reports where other forms of Cu were used [6,7,8], and generally show a decrease in τ with increasing Cu concentration in the CdTe and CdS layers. The increase in τ for the VTD material for ZnTe:Cu thicknesses between 400-2000 Å is still being investigated. However, there is some evidence that trap emission related to Cu incorporation may be affecting the PL decay curves and lifetime values for the VTD samples. It should be noted that all values of τ measured in this second study are relatively long, compared to those resulting from non-optimum temperatures of the first study and shown in Fig. 5. The observation that τ values are lower for the NREL and CSU materials than for the VTD materials may suggest that an optimum temperature for Cu diffusion has not yet been identified for these materials. This is not unexpected because a thorough optimization of the ZnTe:Cu/Ti contact on these source materials has not yet been undertaken.

CONCLUSIONS

This study has shown that the carrier lifetime (τ) within the junction region of a CdS/CdTe PV device can increase or decrease during ZnTe:Cu/Ti contacting

depending upon the amount of Cu that is diffused into the junction and the temperature during contact diffusion. Previous reports that indicate Cu diffusion leads only to reduction in τ may not account for the fact that τ can be longer than as-deposited values when the "optimum" contact temperature is used. This new insight suggests the following sequence to optimize a Cu-containing contact for CdS/CdTe devices: 1) Determine the temperature of Cu diffusion that produces the highest possible value of τ within the junction region. This assessment should be performed at the lowest amount of Cu that can be added to the contact that produces a working device. 2) While maintaining "optimum" contact temperature, add additional Cu to the contact layers(s). This will increase N_A-N_D in the CdTe, increase V_{oc} and reduce W_d. Adding additional Cu to the CdTe will reduce τ from its maximum value, and, depending on the absolute value of τ, voltage-dependant collection (reduced fill factor) may be observed once the space-charge width is approximately equal to the absorption length at MPP. Fill-factor reductions caused by voltage-dependent collection will likely be of a degree that overall device performance cannot be offset by any further increases in V_{oc}. Alternatively, if the CdTe material quality and/or contact process yield a value of τ that remains sufficiently long, it is likely that CdS donor reduction caused by Cu diffusion into the CdS could become the limiting mechanism of device performance.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY) May 2008	2. REPORT TYPE Conference Paper	3. DATES COVERED (From - To) 11-16 May 2008

4. TITLE AND SUBTITLE Effects of Cu Diffusion from ZnTe:Cu/Ti Contacts on Carrier Lifetime of CdS/CdTe Thin Film Solar Cells: Preprint	5a. CONTRACT NUMBER DE-AC36-99-GO10337
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) T.A. Gessert, W.K. Metzger, S.E. Asher, M.R. Young, S. Johnston, R.G. Dhere, and A. Duda	5d. PROJECT NUMBER NREL/CP-520-42558
	5e. TASK NUMBER PVA74303
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393	8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-42558
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) NREL
	11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161

13. SUPPLEMENTARY NOTES

14. ABSTRACT (Maximum 200 Words)

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15. SUBJECT TERMS
PV; carrier lifetime; thin film; solar cells; time-resolved photoluminescence; high-performance device; optimum temperature;

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	UL		19b. TELEPHONE NUMBER (Include area code)

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F1147-E(09/2007)