Thermionic Emission from Cold Electride Films

Richard C. Phillips,[†] William P. Pratt Jr.,[‡] and James L. Dye*,[†]

Departments of Chemistry and Physics-Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

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Thermionic electron emission from 2000−4000 Å thick films of K^+(cryptand[2.2.2])e^- and Rb^+(cryptand[2.2.2])e^- was studied as a function of temperature and time. The total charge collected was generally several hundred nanocoulombs with peak currents in the range of 5−100 pA. Although electron emission was not a *direct* result of thermal decomposition of the films, the peak current correlated with the decomposition rate. At a given temperature, the current increased gradually to a peak value and then decreased to near zero. Interrupting the process by cooling before complete decay, followed by a return to the same temperature, restored the previous current−time behavior. Once the current had decayed to near zero, the only way to restore emission was to raise the temperature above the previous value. The process of growth and decay was then repeated. The origin of emission is unknown, but the behavior suggests the presence of surface defect sites at grain boundaries that are initially empty. Sample decomposition fills these sites, which lie only a few tenths of an electronvolt below the vacuum level. Continued decomposition destroys the sites, but new defect sites can be produced by raising the temperature, probably by forming additional grain boundaries.

Introduction

Low-voltage thermionic emission at ambient temperatures and below is a rare phenomenon. Doped diamond films that have negative electron affinity[1] (NEA) can emit electrons at ambient temperatures provided one can populate the conduction band.[2−6] Field emission from very small tips, such as carbon nanotubes, can occur at relatively low voltages because of the large field gradients at the tip.[7,8] The combination of NEA and field emission from Si/Cs/O nanocluster thin films has recently been demonstrated.[9]

Ten years ago we reported thermionic electron emission from alkalide and electride powders at temperatures as low as −80 °C with cathode to collector voltages of only 2−30 V.[10] Steady-state emission lasted for several hours. For example, a sample of overall composition $Rb^+(15\text{-crown-}5)_2Rb^-$ had a steady-state emission current that ranged from 1.8 pA at −70 °C to 50 pA at −40 °C, with an apparent work function of 0.40 eV. Emission currents as large as 3 nA occurred just after solvent removal. In these cases, the initial emission decayed exponentially over a period of 2−3 min before reaching the steady-state value. Various alkalides and electrides showed this emission behavior. The origin of the emission was not determined, but we suggested that it resulted from the presence of defect states rather than from intrinsic emission from the ground state. The role played by concurrent decomposition of these thermally unstable materials was not known.

A related study was made of the effect of 532 nm laser pulses on subsequent *photoelectron* emission from Na^+(cryptand[2.2.2])Na^-.[11] When this sodide had a relatively high concentration of trapped electrons at sites that normally contain Na^-, the laser pulses populated sites within 1.2 eV or less of the vacuum level. The lifetime of these states was many minutes. By contrast, nearly defect-free samples, prepared by slow crystallization, showed no changes in photoelectron emission after laser pulses. This led us to conclude that empty defect sites, closer in energy to the vacuum level than the ground-state electron sites, are present in rapidly precipitated sodide samples. Furthermore, such sites could be populated with electrons by laser pulses, with only slow depopulation.

In this paper we report the results of systematic studies of thermionic electron emission from solvent-free electride films. These films were prepared by codeposition of the complexant cryptand[2.2.2] (designated C222) and either K or Rb metal. In some of the experiments the rate of bulk thermal decomposition was

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[†] Department of Chemistry.

[‡] Department of Physics-Astronomy.

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monitored by optical absorption spectroscopy and the electrical conductivity was followed by four-probe measurements. Tests with other electrides and alkalides showed that this emission is ubiquitous. Only $Na^+(C222)Na^-$ films showed virtually no thermionic emission. A number of possible models of this behavior were experimentally tested. While the specific nature of the defect sites could not be elucidated, the general behavior of their production, population, and decay was determined.

Experimental Section

The preparation of stoichiometric thin films of $K^+(C222)e^-$ and $Rb^+(C222)e^-$ by high vacuum codeposition of the alkali metal and the complexant onto a sapphire substrate has been previously described in detail.[12–16] By separate control of the oven temperatures and monitoring of the rate of vaporization with quartz thickness monitors, the composition of the films could be controlled to about ±5%. The bell jar was equipped with a rotatable substrate holder that permitted the sample to be moved (after deposition) into positions for the measurement of optical absorption spectra and/or thermionic emission. In some runs the sapphire substrate contained deposited gold electrodes with geometry that permitted the measurement of four-probe electrical conductivity.

Thermionic currents were measured by rotating the sample over a 1 cm^2 collector electrode. This electrode had a 4 mm diameter hole in the center so that the sample could be illuminated with light from a Bausch and Lomb tungsten lamp and single-grating monochromator (400−800 nm). This was used to verify the presence of photoelectron emission and its possible effect on subsequent thermionic emission. An electrometer preamplifier in the vacuum chamber and an external variable-voltage supply were used to measure the emission current and to provide the extracting voltage. The sample was kept at ground potential, and the cathode-to-collector voltage was variable from 0 to +15 V.

The temperature of the sapphire substrate was controlled by regulation of the flow of cold N_2 gas through the copper block that holds the substrate. The temperature of the substrate was within a few degrees of that of the copper block. Equalization of the temperature of the block and substrate required less than 5 min, as determined in test runs with separate thermocouples attached to the block and to the surface of the sapphire substrate. Thus, although the temperatures reported here were measured at the copper block, they are essentially the same as those of the sample.

To be sure that the electrode geometry (four strips of deposited gold film) upon which the electride was deposited did not influence the emission, a number of runs were carried out in which the deposition was made directly onto a continuous gold film. Of course, in these cases, the rate and extent of bulk decomposition could not be monitored by optical spectroscopy and conductivity. The results, however, were similar with either electrode configuration.

When the electride was formed in contact with strip electrodes, three measurements could be made as functions of time and temperature. These were the following: optical absorbance to monitor the extent of bulk decomposition; four-probe conductivities to ensure electrical continuity; thermionic emission currents. Integration of the emission current permitted determination of the amount of charge transferred from the sample to the collector as a function of time. Experiments with the bare substrate, the complexant alone, alkali metal films, and completely decomposed samples yielded no emission currents.

Results and Discussion

Thermionic emission at subambient temperatures has now been observed from the alkalides $K^+(15\text{-crown-}5)_2K^-$, K^+(permethyl peraza-222)K^-, $Rb^+(15\text{-crown-}5)_2Rb^-$, and the electrides $K^+(15\text{-crown-}5)_2e^-$, $Rb^+(15\text{-crown-}5)_2e^-$, $K^+(C222)e^-$, $Rb^+(C222)e^-$, and $Cs^+(18\text{-crown-}6)_2e^-$. Thus, it is a ubiquitous property of these two classes of compounds. As demonstrated by the EPR spectroscopy of powders, the alkalides listed above all have substantial concentrations of defect electrons, in which some of the anionic sites are occupied by electrons rather than alkali metal anions.[17–25] A common feature of both alkalides and electrides is thermal instability above about −60 °C. Over a period of many hours, thin films (1000−4000 Å thick) show decreases in absorbance that result from irreversible decomposition. The process is slow below about −40 °C but is appreciably faster at higher temperatures. The decomposition reaction in a vacuum breaks the $-OCH_2CH_2O-$ linkage to yield ethylene and a glycolate, resulting in loss of the trapped electrons and/or conversion of the alkali metal anion, M^-, to the cation, M^+.[26] It is important to recognize that linkage of thermionic emission to the decomposition reaction cannot be ruled out, since both occur simultaneously. Indeed, the only system that shows little or no thermionic emission is $Na^+(C222)Na^-$. Films with this composition are remarkably stable, even at room temperature.[15]

Our most extensive studies have been made with stoichiometric films of $K^+(C222)e^-$ and $Rb^+(C222)e^-$ between 2000 and 4000 Å thick. Results with other alkalides and electrides are qualitatively similar. The general behavior is illustrated in Figures 1 and 2, which show both the emission current and the temperature as functions of time after preparation of the film. The experiment leading to Figure 1 was carried out with a series of temperature increases, each interrupted by a decrease in temperature. Figure 2 by contrast, refers to stepwise increases in temperature without any intervening decreases in temperature. These two experiments are typical of 22 separate runs made with a variety of temperature−time profiles. Tables S1 and S2 in the Supporting Information provide summaries of the results from all runs.

As a general result of the various experiments we can draw the following conclusions:

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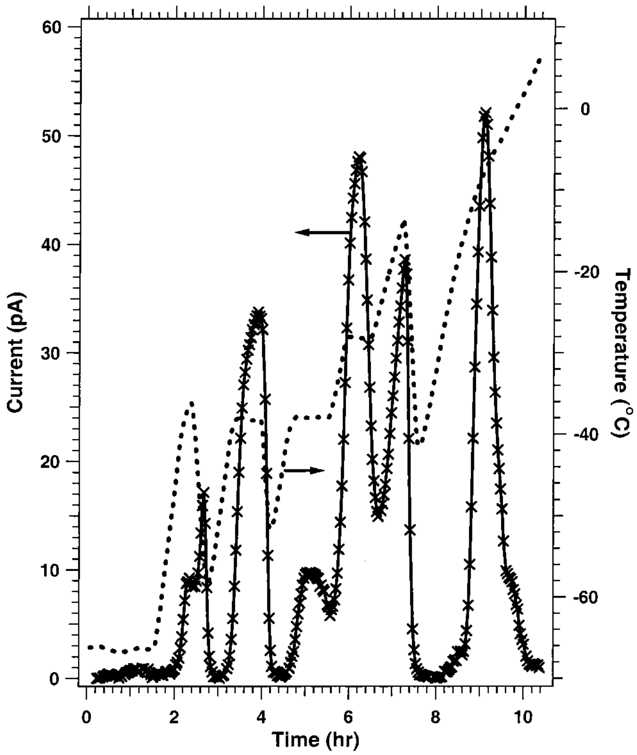

Figure 1. Thermionic emission current from a 2760 Å thick film of K$^+$(C222)e$^-$ (run of 04/01/98, formed at −66 °C) as a function of time and temperature. The temperature (dashed line) was alternately raised and lowered. Note particularly the depletion of emission at −38 °C shown by the first three peaks and the complete absence of emission upon return to −40 from −14 °C (at 7.2 h after deposition).

1. There is little or no emission at temperatures below about −50 °C, either initially or later. Interruption of emission at higher temperatures by cooling to this temperature or below eliminates or drastically reduces the emission current. This behavior is shown in Figure 1. The shut-off of emission upon cooling implies that the emitting states lie below the vacuum level. Although we cannot separate the effects of temperature on decomposition and emission, the previous results[10] suggested that the effective work function is in the range 0.2−0.5 eV.

2. Upon increase of the temperature some minutes after the film has been prepared there is a substantial delay between the temperature increase and the rise of the emission current. Again this is clearly shown in Figure 1, where there is a lag of 30 min between the initial temperature increase to −40 °C and the peak emission current. The time delay between the establishment of a constant temperature and the observation of peak emission at that temperature varies from run to run. However, the delay ranges from 2 to 30 min. Another example is shown in Figure 2, where the emission current only begins to rise appreciably after 60 min at −43 °C. Clearly, the increase in emission current lags the increase in temperature. This indicates that the concentration of defect electrons responsible for the emission increases slowly following an increase in temperature.

3. At constant temperature, the emission current reaches a maximum and then slowly decays to a near zero value. The first three peaks in Figure 2 illustrate this behavior. Even though bulk decomposition during one of these periods can be as little as 5%, the emission gradually dies away. This suggests that the concentration of defects near the surface that can accept electrons to give thermionic emission is limited and that the defects are gradually removed or rendered inactive upon standing at constant temperature for a time period of 10−20 min.

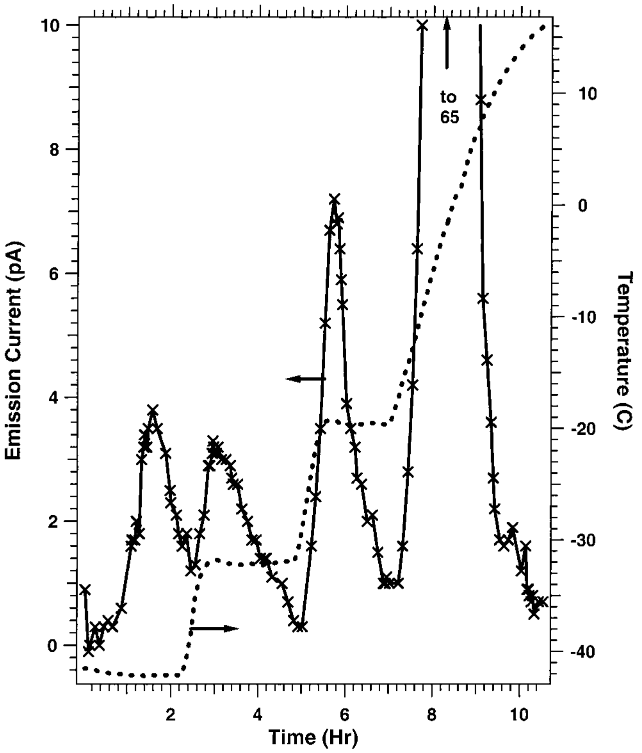

Figure 2. Thermionic emission current from a 3430 Å thick film of K$^+$(C222)e$^-$ (run of 12/01/97, formed at −42 °C) as a function of time and temperature. The temperature (dashed line) was increased and then held constant for a period of time before being increased again. Note that, in all cases at constant temperature, the emission current grew to a maximum and then decreased slowly to a low level. Note also that the initial emission growth at −42 °C was delayed by ~1 h after formation of the film.

4. When the temperature is reduced before the emission has decayed, so that the emission current at the lower temperature is low or zero, followed by a return to the same higher temperature, emission resumes to complete the time course noted under conclusion 3 above. The first three emission peaks in Figure 1 illustrate this behavior. The temperature (initially −66 °C) was increased to −38 °C three times, with intermediate cooling to −60 and −50 °C. In other runs, maintaining the temperature at about −40 °C for a longer time resulted in decay of the emission to zero. This shows that while the number of populated or available defects at a given temperature is limited, cooling the sample preserves them for future emission.

5. As shown by both Figures 1 and 2, after emission has ceased (whether the sample has been cooled or not) raising the temperature to a new level, even as little as 10 deg above the previous emission temperature, starts the process again. Slow growth of emission followed by a maximum and then decay to zero or near zero occurs each time the temperature is increased to a new level. This behavior persists until the film has completely

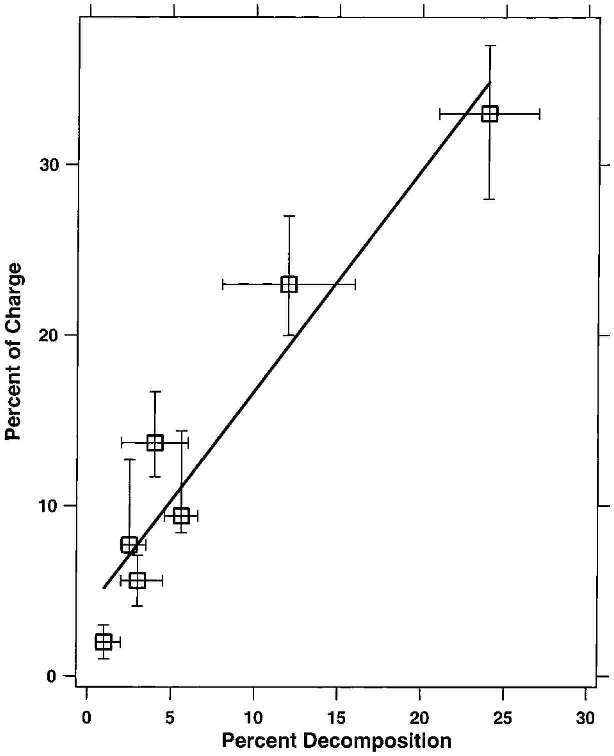

Figure 3. Correlation between the percent of the total charge emitted during the first emission peak at ~ −40 °C and the estimated percent decomposition of the bulk film during that time. The latter was obtained from the decay of the absorbance with time. The behavior at later times (and higher temperatures) was qualitatively similar, but the effects of decomposition and temperature could not be separated.

decomposed. This effect of temperature is unusual, unexpected, and difficult to explain, but it has been verified many times. We are forced to conclude that an increase in temperature produces new defects (or "rejuvenates" old ones) that can be slowly populated with electrons. But, as in the initial emission, the number of such defects is limited and their lifetime is finite.

6. In five runs with $K^+(C222)e^-$ and two runs with $Rb^+(C222)e^-$, the thermal decomposition rate was monitored by optical absorption spectroscopy. As shown in Figure 3, the percent of the total charge transferred *during the first emission peak(s) at* ~ −40 °C and the percent decomposition values that accompany this first emission are strongly correlated. When the extent of decomposition is low, the charge emitted is small, while more extensive decomposition leads to greater emission. The same trend is observed later in the runs, but it is difficult to separate the effects due to decomposition from those caused by increased emission at higher temperatures. Thus, it is clear that defects are populated with electrons by decomposition, even though continued decomposition at constant temperature does not prevent the thermionic current from decreasing to zero or near zero. In one run with $Rb^+(C222)e^-$, the film was remarkably stable and even after 2.8 h at −60 to −80 °C and 1.0 h at −40 °C only 2% of the total charge was emitted. During this time less than 2% decomposition occurred. Substantial emission was observed only when the temperature was increased to −25 °C.

7. The time course of thermionic emission before and after interruption of current collection is the same. That is, the variation of emission current with time is not affected by setting the bias to zero (except that *during* this period the emission current drops to zero). After resumption of collection, the current−time curve is a continuation of what it would have been had the bias voltage remained on. This shows that removal of electrons by emission has a negligible effect on the population of defect electrons. This may be because only a small fraction of the defect electrons are emitted or because empty traps are rapidly refilled.

8. There is no apparent correlation between the thermionic emission current and the electrical conductivity of the films. Although $K^+(C222)e^-$ and $Rb^+(C222)e^-$ are rather conducting, emission was also observed for insulting films such as $Cs^+(18C6)_2e^-$. Evidently, the emission currents are low enough and the conductivities are high enough that there is no problem with deviations from overall neutrality.

9. The total charge emitted is in the range of tens to hundreds of nanocoulombs. Even if the collected emission current only occurs for emission sources within 50 Å of the surface (a likely value of the range of unscattered electrons), only about 1% of the electrons contained in this surface layer are emitted during the entire process. If electrons released deeper in the sample migrate to the surface, this percentage is even smaller. How many defects are occupied is unknown, however. The emission current is only indicative of the *relative* concentration of occupied defect sites at a given time. The fraction of sites which emit electrons could be small. Alternatively, sites that are refilled during the lifetime of the defect could yield total emissions that exceed the number of sites.

10. As in the previous study (see Figure 2 of ref 9), the emission current rises rapidly as the bias voltage is increased and then more slowly for bias voltages above about 10 V. The 15 V maximum available with this equipment limited this study. Reduction to zero or negative bias yielded zero emission current. That electrons rather than negative ions are emitted was shown in the previous study.[10]

11. Illumination of the films with visible light over the wavelength range 400−800 nm, even at temperatures as low as −60 °C, produces immediate photoemission currents that return to zero when the light is turned off. Films that have not decomposed significantly show a larger photoelectric response. This decrease in the photoemission current suggests that surface decomposition or reaction may tend to block electron emission. It should be noted that the bulk absorbance of the films in the visible region is less than 1.0, whether fresh or decomposed. Therefore, photons can penetrate the entire sample. However, we would anticipate rather short mean free paths of electrons excited by light absorption in the interior of the film.

Thermionic emission of electrons from electrides and alkalides probably occurs from defect or surface sites that lie only 0.2−0.5 eV below the vacuum level. These sites are either not initially populated or not initially present in vapor-deposited films, although they are prevalent in freshly formed powders or films that are made by solvent evaporation of alkalide/electride solutions.[10]

The correlation of the thermionic emission current with decomposition shown in Figure 3 shows that decomposition plays a role in either the production of defect sites or in filling preexisting defect sites with electrons (or both). Electron emission does not occur *directly* as a result of the decomposition reaction (chemiemission) because the emission current is delayed upon raising the temperature. Also, even as decomposition continues at a fixed temperature, the emission current decreases to nearly zero. Once this occurs, the only way to renew emission is to raise the temperature to a value above that at which emission previously occurred.

Decomposition could either produce *and* populate defects or could populate preexisting defects. In any event, the number of such sites is limited and their lifetime after population is finite. Decreasing the temperature before all emitting defects have been eliminated "preserves" the defects for many minutes, but upon return to the previous temperature, the emission only slowly grows to a maximum. This suggests that "empty" defects can exist and that they can be filled with electrons when decomposition resumes.

Since decomposition plays a role, it is appropriate to review what is known about the chemistry involved. The counterions in electrides and alkalides, which are trapped electrons and alkali metal anions, respectively, are powerful reducing agents and attack the O−C bond in crown ethers and cryptands to produce ethylene (during constant evacuation) and two alkoxide groups.[26] In a closed tube under static vacuum, ethane and butane are also formed.[26] When compounds such as $K^+(C222)e^-$ decompose, we expect the dialkoxide product to attract K^+ from a neighboring complex. Since two electrons are required to form ethylene, each reacting cryptand molecule leaves behind an intact cryptand, with or without K^+ trapped inside. The decomposition reaction is highly exothermic, with sufficient energy (∼2 eV as determined from DSC studies) to produce electrons in excited states if the decomposition is properly coupled to adjacent trapping sites. There appears to be no way from the available data to determine whether the decomposition reaction *produces* the defect sites and subsequently populates them or just *populates* existing defect sites. Thus, we can only speculate about possible mechanisms, ruling out those that conflict with the 11 facts described previously. Some of the possible scenarios have already been ruled out by one or more of the observations and have been handled already.

(1) Accelerated Surface Decomposition/Reaction. The decay of the optical spectrum with time monitors only *overall* decomposition. Surface sites may be more subject to decomposition and could also react with residual gases such as water vapor. Thus, at a given temperature, the active emitting sites on the surface, produced or filled by decomposition, could be prevented from emitting electrons by a thick enough layer of decomposition products. Thus, the buildup of active sites could proceed until the surface layers had decomposed enough to form a film that prevented electron escape.

There are at least two problems with this model. First, it requires that the layer responsible must survive cooling and heating to the same temperature but form a new nonblocking surface at a slightly higher temperature. Second, rapid decomposition, which would be expected to form such a layer quickly, instead leads to greater emission, especially at higher temperatures. These two problems disfavor the blocking of emission from occupied defect sites by a simple physical barrier to electron emission.

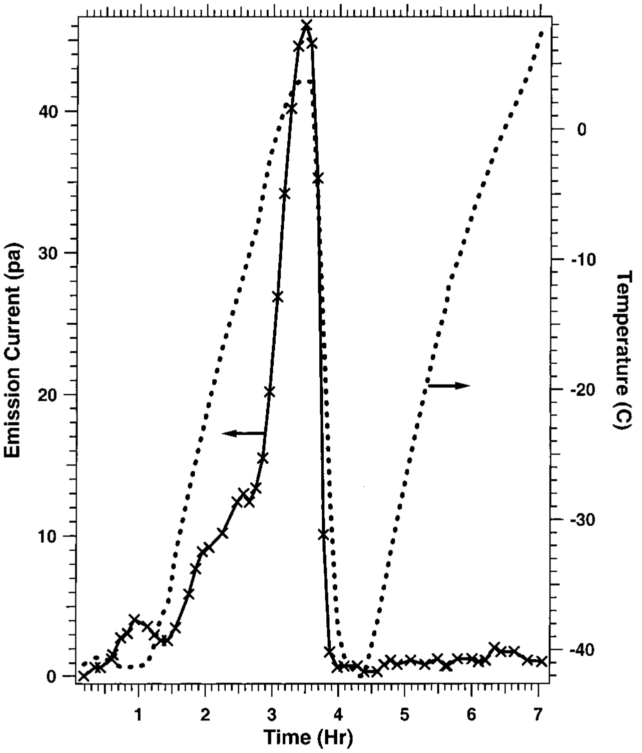

Figure 4. Thermionic emission current from a 3140 Å thick film of $Rb^+(C222)e^-$ (run of 10/06/97, formed at −41 °C) as a function of time and temperature. After 1.2 h at −41 °C, the temperature was ramped to +4 °C. Note the continued large growth in emission. The absence of emission after this temperature excursion indicates that the film had decomposed completely.

(2) Saturation of Preexisting Defect Sites. If the role of decomposition is to populate surface defect sites that are already present, and if the adjacent decomposition product eventually "kills" the defect site, then the growth and decay of thermionic emission at constant temperature would result naturally. This model would also explain the ability to resume emission upon a return to the previous temperature after cooling, as long as some defect sites remain. The model requires, however, that *new* defect sites can be generated or exposed, merely by raising the temperature above the previous value. For example, Figure 4 shows that continuously raising the temperature produces a large emission current that continues to grow until the bulk of the sample has decomposed. Yet, the inability to produce new defect sites by a cooling, warming cycle that merely returns to the old temperature shows that just heating a sample does not restore defects that have been deactivated. The sample seems to retain a "memory" of its previous thermal history.

(3) Defect Sites at Grain Boundaries. Impedance spectroscopy studies of $K^+(C222)e^-$ powders show that the capacitance of the sample is many times higher than the simple electrode geometry would suggest.[27] This indicates the presence of resistive grain boundaries that impede electron flow. Perhaps such grain boundaries are prime locations for defect sites that are responsible for thermionic emission when populated by the decomposition reaction. Differences in the thermal expansion coefficient of sapphire and the sample could result in the formation of more grain boundaries as the sample is heated. The observed effect of temperature cycling would require that simply cooling and reheating to the previous temperature would not produce many *new* grain boundaries, whereas further heating would do so. In this way, heating would increase the effective “fresh” surface area and also the number of defect sites.

(4) Field Emission at Sharp Points. If the film surface is rough enough to produce hills and valleys with curvature on the submicron scale, the field gradient at sharp features could be high enough to permit electron emission from states at energies well below the vacuum level. This model would require “annealing” of such features at constant temperature and the production of new sharp features when the temperature is increased. The absence of emission from stable films would seem to rule out this model as a complete explanation. It is possible, however, that surface roughness could permit emission from deeper traps and could yield an effective distribution of energies from which emission could occur.

Conclusions

The exact cause of the unusual low-temperature, low-voltage thermionic emission of electrons from alkalides and electrides remains a mystery. The most plausible scenario is the presence of initially empty surface defect sites at grain boundaries. Electrons added to such sites lie only a few tenths of an electronvolt below the vacuum level. Decomposition of the sample both fills these sites and subsequently eliminates them. Increasing the temperature produces new defect sites, probably by forming additional grain boundaries or by exposing new surfaces due to sample cracking.

Obviously, electron emission from a decomposing sample is of little practical use. It may, however, point the way to more stable cold electron sources. This work and the photoemission studies[11] of $Na^+(C222)Na^-$ suggest that preexisting defect sites in alkalides and electrides might be filled by photoexcitation. The intensity of the visible light used in the present study was much lower than that of the laser pulses used in the previous photoemission experiments.[11] As a result, photoelectron emission was observed in the present work, but the light intensity was not high enough to significantly populate empty defect sites. If we had a thermally stable electride, preirradiation with intense light might populate defect sites close enough to the vacuum level to yield both infrared photoelectron emission and thermionic emission. However, the electrides available to date are thermally unstable, even in the dark. Thus, it is not easy to distinguish thermionic emission due to photolytically populated states from that caused by sample decomposition. The recent synthesis of two thermally stable alkalides with the aid of permethylated peraza complexants[28] provides hope that thermally stable electrides may yet be synthesized.

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Supporting Information Available: Two tables giving the temperature−time profiles of emission for all runs and, where available, the percent decomposition. This material is available free of charge via the Internet at http//pubs.acs.org.

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