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Low Temperature Cathodoluminescence of Space Observatory Materials

Amberly Evans, Gregory Wilson, Justin Dekany and JR Dennison

Abstract—In recent charging studies, a discernible glow was detected emanating from sample surfaces undergoing electron beam bombardment that resulted from a luminescent effect termed cathodoluminescence. This suggests that some of the materials used as optical elements, structural components, and thermal control surfaces in the construction of space-based observatories might luminesce when exposed to sufficiently energetic charged particle fluxes from the space plasma environment. A central focus of our experiments was the temperature dependence of the luminescent behavior. Here, an overview of our experimental results is given, as well as a qualitative model to describe the luminescent behavior. We look at a simple model of band theory and the filling of localized or trapped states and the electron transitions from which the luminescence originates.

Index Terms—luminescence, electron flux, space environment interactions, materials testing, low temperature

I. INTRODUCTION

During charging studies using a low-flux intermediate-energy electron beam, thin film highly disordered silicon dioxide (SiO_2) samples exhibited a cathodoluminescent behavior. Similar behavior has been observed in other experiments at Utah State University (USU) for other materials including carbon composites and polymers. Previous studies have observed similar cathodoluminescence in both epoxy resin composites [1]-[3] and in disordered SiO_2 [4], [5] however little information is available with regard to the temperature dependence of the cathodoluminescence. These results suggest that materials used in structural components, optical elements, and thermal control surfaces of spacecraft and space-based observatories could, when exposed to the space plasma environment, luminesce. If these visible, infrared and ultraviolet emissions are intense enough, they could potentially produce optical contamination detrimental to the performance of the observatory optical elements and sensors, and act to limit their sensitivity and performance windows. As future observatory missions push the envelope into more extreme environments and use more complex and sensitive detectors, a fundamental understanding of the

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dependencies of luminescent intensity on time, temperature, incident electron flux and energy, and material structure becomes critical.

II. EXPERIMENTATION

Experiments were conducted in the main USU electron emission ultrahigh vacuum test chamber [6], modified for observations of low intensity UV/VIS/NIR glow over a broad range of sample temperatures [7]. Figure 1 provides a general schematic of the experimental system used.

A low energy electron gun [Staib, EK-5-51] delivered a well-characterized, low-flux beam (typically $\sim 50 \text{ pA/cm}^2$ to $1 \mu\text{A/cm}^2$) over an energy range of 20 eV to 5 keV. For results shown in Figs. 2 and 3, beams of 5 keV at $\sim 500 \text{ nA/cm}^2$ were used. The defocused electron beam produced a beam profile at the sample with about $\pm 30\%$ uniformity over an $\sim 3 \text{ cm}$ diameter beam spot. Beam fluxes were monitored with a Faraday cup. The W filament of the electron gun also produced visible light that traveled down the bore of the electron gun and impinged on the sample; even at the low operating filament temperatures used for the low flux beam (2500K), the intensity of the filament spot on the sample was larger than the observed luminescent signals. To minimize this contaminating filament light, a blocking aperture was developed, which allowed an electron beam focused $\sim 5^\circ$ off axis and then electrostatically deflected back on to the sample while sending the filament light into an optical baffle. The baffle and the primarily specular nature of the reflected

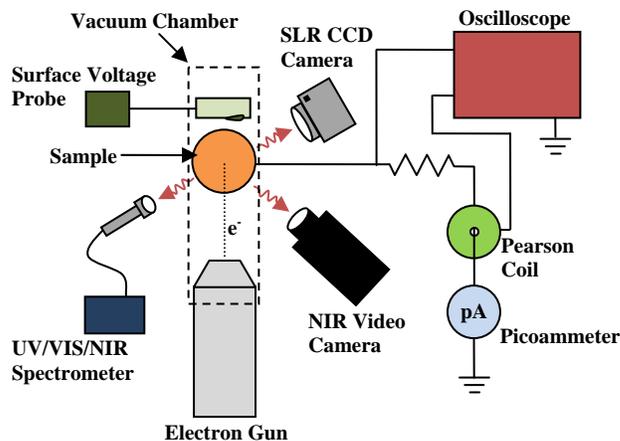


Fig. 1. Block diagram of instrumentation for collecting the pulse charging surface voltage, electrode current and cathodoluminescence data induced by electron beam bombardment. Instrumentation includes picoammeters, Pearson coils, and a storage oscilloscope for electrode current measurements and UV/VIS and IR spectrometers, an SLR CCD still camera, and a NIR video camera for optical measurements.

filament light that made it past the blocking aperture reduced the stray light contamination seen by the optical cameras to acceptable levels.

Two cameras and two fiber optic spectrometers were used to monitor low light intensity. Optical data were collected using UV/VIS (Stellarnet, 13LK-C-SR; ~ 200 nm to 1080 nm with ~ 1 nm resolution) and NIR (Stellarnet, RW-InGaAs-512; ~ 1000 nm to 1700 nm with ~ 3 nm resolution) spectrometers, an SLR CCD still camera (Cannon, EOS Rebel XT DS126071; ~ 400 nm to 700 nm, 30 s per frame), and a VIS/NIR video camera (Xybion, ISG-780-U-3; ~ 400 nm to 900 nm, 30 frames per s). Additional InSb (~ 1000 nm to 5500 nm) and InGaAs (~ 800 nm to 1700 nm) video cameras and filter combinations were used to monitor IR emissions; no IR in the 900 nm to 2500 nm range was observed for any of the experiments reported here. Prior to the luminescence studies, the spectral response and range were determined and the sensitivity of the instruments was calibrated with NIST traceable sources.

The sample carousel was thermally anchored to (but electrically isolated from) a thermal reservoir. In combination with resistive heaters and liquid N₂ cryogen, the samples were maintained over a range of temperatures from ~ 150 K to ~ 400 K with a long-term stability of ± 3 K.

Samples (2.5 cm diameter) of optically smooth, thin film (~ 65 nm thick) disordered SiO₂ (fused silica) deposited on ~ 175 nm thick highly reflective, optically smooth metal (mostly Au) layers on a 2 mm thick fused quartz substrate. The samples were optically cleaned and underwent a ~ 12 hr vacuum bakeout at ~ 390 K and $< 1 \cdot 10^{-3}$ Pa to eliminate adsorbed water and volatile contaminants. The samples were mounted on Cu pedestals on a multi-sample carousel, and were placed in an ultrahigh vacuum chamber (base pressure $< 1 \cdot 10^{-6}$ Pa) for > 24 hrs outgassing before measurements were made. Though not the focus of this paper, each sample was wired appropriately for collecting electrical data during bombardment as well; these results are reported elsewhere [8].

III. RESULTS

The thin film SiO₂ samples exhibited readily observable luminescence, as shown in Fig. 2. The intensity scaled with electron beam intensity and responded to changes in beam position and profile on rapid time scales, as demonstrated by the image of a defocused and distorted electron beam incident on the sample shown in Fig. 2(d). A clear variation in the intensity and color as a function of temperature was seen with the SLR images Figs 2 (a-c); as temperature increased, the light emission from the samples became bluer and less red. This was confirmed with relative intensity measurements of the Red-Green-Blue bands of the CCD camera as a function of temperature, as in Fig. 3(a). Overall intensity of the glow in the visible range—as measured with the CCD video camera—increased from room temperature to the lowest measured temperatures at 163 K.

The spectral dependence of the luminescence at room temperature is shown in Fig. 3(b). Three peaks are observed, centered at approximately 275 nm, 500 nm and 645 nm; an additional shoulder is observed at ~ 455 nm results. These peaks were consistent with the results of Sahl and Trukhin in

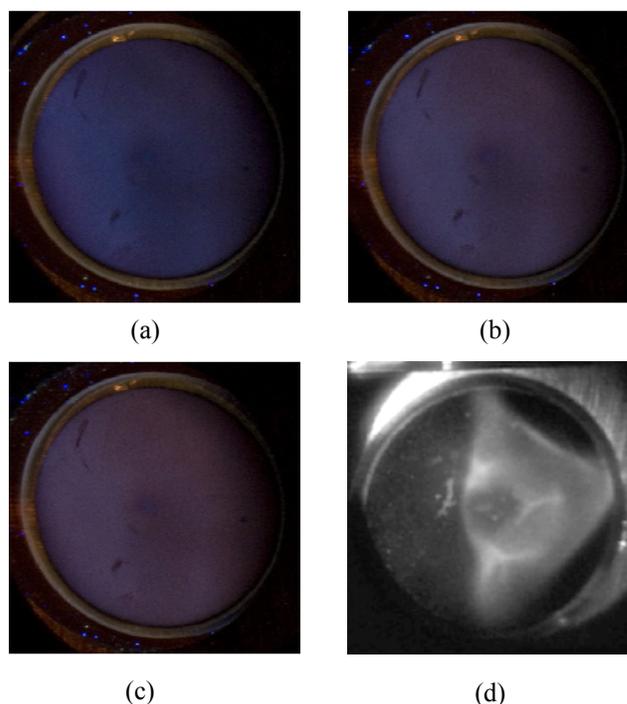


Fig. 2. Optical images of luminescent SiO₂ samples. SLR still images of the glowing thin film SiO₂ sample at (a) 273 K, (b) 193 K and (c) 163 K. Note that the lower temperature image has a very red tint to it. However, as the temperature continues to rise, and eventually reach room temperature, the color begins to shift to blue. (d) CCD video camera frame showing the luminosity produced by a highly distorted, defocused electron beam.

similar disordered SiO₂ samples at room temperature [4], [5]. Sahl identified the peak at 645 nm as a nonbridging oxygen hole center in the structure. The peaks at 275 nm and 500 nm are results of an oxygen deficient center, as identified by Trukhin (see Fig. 5)

The variation in spectra intensity with temperature is shown for three representative temperatures in Fig. 3(b and c). The observed decrease in the red peak near 645 nm and the increase in the blue and UV peak near 455 nm and 275 nm, respectively, are consistent with the qualitative SLR observations seen in Fig. 2. In Fig. 3(d), a downward shift in wavelength with increasing temperature is observed.

IV. BAND THEORY OF HIGHLY DISORDERED INSULATORS

The basic theory behind the observed luminescence phenomenon observed here is the band theory of highly disordered solids. In basic band theory, the energy levels of individual atoms coalesce, forming a continuum of energy levels as the atoms are brought closer together thus creating a solid structure (see Fig. 4). The number of levels created in a given band is the number of energy levels originally available, typically one per atom in the solid. Thus, as the number of atoms increases, so do the number of new energy levels, eventually creating a continuum of energy levels for the electrons in our new structure to fill. This continuum is called an energy band. Within a molecular or crystalline structure, many energy bands are formed and are filled, starting at the band of lowest energy. The extent to which these bands are filled is how solids are classified as conductors, semiconductors and insulators.

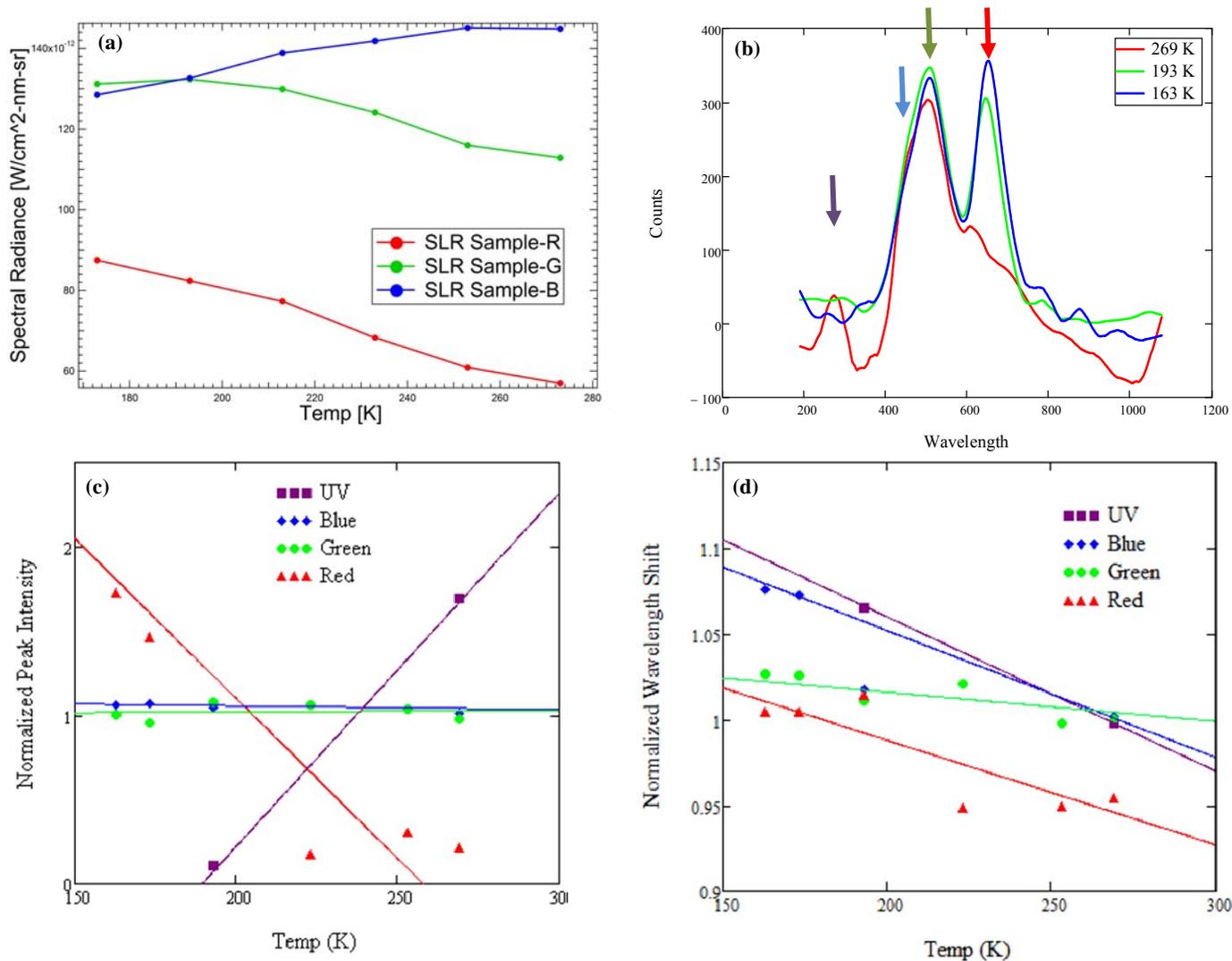


Fig. 3. (a) Variation with sample temperature of the Red-Green-Blue components of the SLR still CCD camera image average intensities across the glowing thin film disordered SiO₂ sample. (b) Three glow spectra at decreasing sample temperature, measured with the UV/VIS spectrometer. Four peaks are identified in the spectra at nominal wavelengths of ~275 nm, 455 nm, 500 nm, and 645 nm. (c) Normalized peak amplitudes as a function of sample temperature of the red (~645 nm), green (~500 nm), blue (~455 nm) and UV (275 nm) peaks. These are calculated as the amplitude of each peak (with baseline subtraction) normalized by the room temperature amplitudes. (d) Normalized peak position as a function of sample temperature of the red (~645 nm), green (~500 nm), blue (~455 nm) and UV (275 nm) peaks.

The Fermi energy of a material is the energy of the highest filled state at absolute zero; the Fermi level, ϵ_F , is the (weakly) temperature dependant chemical potential defined as the energy for 50% probability filling a state. If, as in our experiments, electrons are added to the material by, say, electron bombardment, these new electrons will start to fill up higher energy levels, thus creating what is termed an effective Fermi level, ϵ_{eff} ; this can be thought of as a charge- (and temperature-) dependant chemical potential.

Conductors are materials with partially filled energy bands. Because the bands are not completely filled, the electrons that occupy that band have high mobility, allowing electrons to move freely; thus, conductors are electrically conductive. Insulators have a fully filled valence band and a large band gap to the conduction band, such that even with large amounts of thermal energy, valence band electrons have an extremely low probability of being thermally excited into the conduction band. So, electrons in insulators have very little mobility, making these materials electrically insulating. For intrinsic

insulators and semiconductors with no defect states, the Fermi energy is at the middle of the band gap. Semiconductors have two bands that are separated by a small amount of energy so that, with sufficient thermal energy, electrons in the valence band have a small but significant probability of excitation into the higher bands, therefore leading to moderate conductivity (see Fig. 4).

SiO₂ is an insulating material that has a band gap of about 8.9 eV. Hence thermal excitation from the valence to conduction band is highly improbable; the only likely source of such excitation is through collisions of the incident high energy electrons. Since visible light is in the 1.65 to 3.1 eV range, even if electrons in the valence band of SiO₂ were electronically excited to the conduction band, no visible light (only high energy UV radiation) would be emitted upon relaxation or recombination of the excited electron with an empty state in the valence band (termed a hole). Thus, there must be other states for the electrons to reside in within the band gap; there must be localized defect or “trap” states.

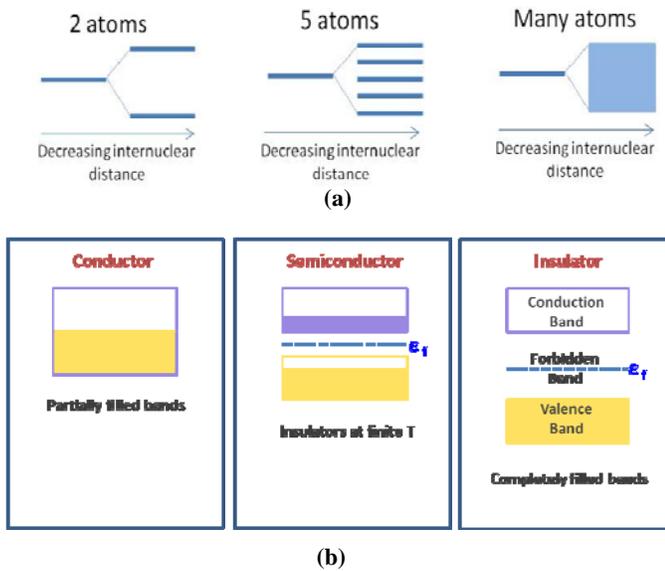


Fig. 4. (a) The combination of energy levels creates new energy levels, eventually leading to a band of energies available for electrons to occupy. (b) Classification of solids as conductors, insulators and semiconductors as determined by the extent of the band filling. Note the position of the Fermi energy, E_F .

The localized states in disordered SiO_2 are due to defects in the crystalline structure or chemical defects from possible substitutional dopants. These defects add energy states within the forbidden band (see Fig. 5). Now, when valence band electrons are excited into the conduction band by the high energy incident electron radiation and then relax, there are now ‘closer’ (in energy) trap states that the electrons can relax to. Some relaxation processes are photon emitting processes. Therefore, if these processes are in the appropriate energy range, visible photons will be detected, whether it be with our eye or other visible or IR range detecting instruments. These light emitting defect structures, or chromophores, can be inherent in the material or can be induced by electron beam bombardment. In other words, our experiments or the space plasma may create these defects which then cause them to luminesce.

V. TEMPERATURE DEPENDANT CATHODOLUMINESCENCE MODEL

A model with multiple bands of disordered states in the band gap has been developed to qualitatively explain the temperature dependence of the observed luminescence spectra. The presence of four identifiable peaks in the spectra suggest that there are at least four bands of optically active state, as shown in Fig. 3, with energy separations determined by the energy of the emitted photons. Because transitions from an extended state in the conduction band to a localized disordered state are, in general, much more likely than between two localized disordered states with mean separations greater than the spatial extent of the localized states, we expect the four bands to be at ~ 1.93 , ~ 2.48 , ~ 2.76 , and ~ 4.97 eV below the conduction band edge.

To model the temperature dependant behavior of the peak intensities, we need to model the extent and occupancy of these disordered bands. The intensity of a given band will be

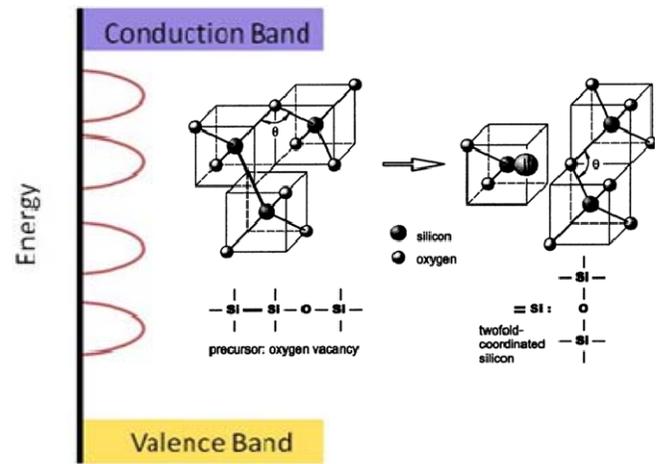


Fig. 5. A diagram of the energy bands of a material with Gaussian trapped states within the band gap. These trapped states are created by defects in the structure. One example of such a defect found in disordered SiO_2 is shown at right [ref]. This shows an oxygen deficient center in the structure the site of the chromophore.

proportional to the number of excited electrons in the CB, the number of available, optically-active states in the disordered band, and a transition probability (or equivalent capture cross section). The occupancy of a given state is determined to first order by the effective Fermi level for a given density of trapped charges. A more detailed model will take into account the transition probabilities from one trap state to another driven for the most part by thermal transitions.

We begin with a two band model for the peaks at ~ 275 nm and ~ 645 nm, as shown in Fig. 6. In this model, the band generating red photons has available, optically-active states at an energy $\epsilon_{\text{red}} \sim 1.93$ eV below the conduction band edge. A similar band generating the ~ 275 nm photons is centered at $\epsilon_{\text{blue}} \sim 4.97$ eV below the conduction band edge. At different temperatures, the varying amounts of thermal energy control the thermal excitation of the electrons and the relative filling of the bands. These thermal excitations will fill available energy levels in some energy bands, while vacating levels in the other. This is the origin of the different photons being emitted.

At absolute zero (see Fig. 6(a)), no electrons will occupy levels above the effective Fermi level. Therefore, excited electrons can only relax into states in the red band, emitting lower energy red photons. At low temperatures with $0 < k_B T \ll (\epsilon_{\text{red}} - \epsilon_{\text{uv}})$ (see Fig. 6(b)), a significant number of electrons in the UV band (represented in blue in the figure) are thermally excited to the red band (either directly or through an intermediate excitation into the conduction band). This creates empty states in the UV band that can then accept electrons decaying from the conduction band and generating higher energy UV photons. Thus significant numbers of electronically excited electrons can now relax from the conduction band into either the red or UV bands; the relative intensities of the red and UV emission depends on the relative number of unoccupied states in the two bands and the transition probabilities into these two bands from the conduction band. There is also a weaker dependence on the transition from red band states directly into UV band states and for recombination of electrons in the red and UV band with largely immobile holes in the valence band. At higher

Disordered Insulator

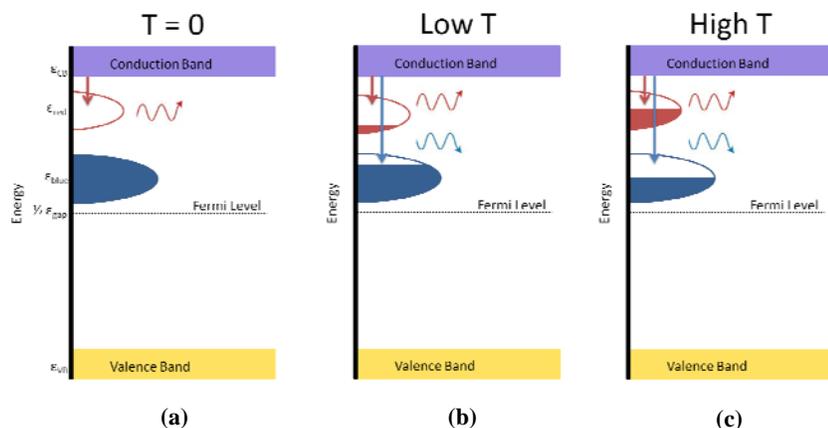


Fig. 6. Qualitative model of occupied densities of state as a function of temperature during cathodoluminescence. (a) At absolute zero, no electrons occupy levels above the effective Fermi level. Therefore, excited electrons can only relax to the red state, emitting red photons. (b) If a little bit of thermal energy is added to the system, some UV band electrons (represented in blue) are excited to the red band, thus, electronically excited electrons now relax to either the red or UV bands. (c) Here, we see the same effect as in (b), only it is more enhanced. Therefore, we see more UV photons being emitted from the material.

temperatures $0 \ll k_B T < (\epsilon_{\text{red}} - \epsilon_{\text{uv}})$ (see Fig. 6(c)), even more electrons from the UV band are thermally excited into the red band. At high enough T , if the decay time of electrons from sites in the red band into the UV band is longer than the trapping of electrons excited into the conduction band by incident high energy electrons, a population inversion can occur as seen in a 3-level laser system.

Earlier we discussed a wavelength shift with temperature; that is, with increasing temperature, peak wavelength decreased (see Fig. 3 (d)). From our model, this behavior is predicted in the UV and blue regions however, according to our model, the red peak should increase in wavelength. Looking specifically at the UV band, at low temperature, only high energy levels are available for electron relaxation within that energy band. As temperature increases, lower energy levels become available. So going from lower to higher temperature, the energy of the emitted photons increases and thus, the peak wavelength decreases and a shift appears in the spectra. A weakness in our model appears when we look at the behavior of the red band, in which we expect the wavelength to increase. But, as seen in Figure 3(d), it decreases. This breakdown in our model could be due to thermal excitations in the red band or even the presence of more than one available red band.

VI. CONCLUSIONS

Low intensity cathodoluminescence was observed for disordered SiO_2 thin films under low intensity incident electron irradiation. The observed number and wavelengths of the observed peaks were consistent with previous room temperature observations. The intensity and peak positions of the primary peaks observed in the UV/VIS/NIR region were measured as a function of temperature from ~ 160 K to ~ 280 K. A model based on multilevel disordered peak DOS qualitatively explains the intensity versus temperature and wavelength versus temperature trends observed.

The next steps in this research involve measurements at lower T down to ~ 40 K and at higher (< 400 K) temperatures. We intend to develop a quantitative model for intensity vs T and wavelength vs T behavior for all four of the observed luminosity peaks. In principle the luminosity measurements can be used to map the distribution and magnitude of the various DOS for the different bands. Investigations of the

luminescent intensity versus incident electron energy and beam current density, incident electron range, and film thickness are in progress. Through measurements of intensity versus electron beam exposure time and the decay time after turning the electron beam off we hope to study initial time dependence as traps fill to the effective Fermi level and as traps empty after excitation into the conduction band by the high energy electron irradiation has ceased.

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Greg Wilson is currently a graduate student at Utah State University in Logan, UT pursuing an MS in physics. He received BS degrees in physics and mathematics from USU in 2011. He has worked with the Materials Physics Group for two years on electron emission and luminescence studies related to spacecraft charging. He also developed a composite model for electron range over a wide range of incident energies applicable to diverse materials.



Justin Dekany is currently a graduate student at Utah State University in Logan, UT pursuing an MS in physics. He received a BS degree in physics from USU in 2010. He has worked with the Materials Physics Group for four years on electron transport measurements, electrostatic discharge tests, electron emission measurements, and luminescence studies related to spacecraft charging. He has been the Lab Manager for the Materials Physics Group for the last two years.



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