Optically reversible photochromism in natural pink diamond

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ABSTRACT

Naturally occurring pink diamonds include defect centers with properties that differ greatly from those of commonly synthesized diamond centers. The pink diamond color-center demonstrates optically-controllable photochromism which is stable at ambient temperatures. The nature of this defect and the origin of the photochromism are yet to be explained. In this work we show that the photochromic behavior can be explained by competing photoionization processes at multiple defect centers in response to an applied optical pump. Our approach quantitatively explains the dependence of both the response rate and the resulting color on the pump wavelength. From measurements of the photochromic response we are able to extract parameters that describe the ionization cross-sections of the involved centers.

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1. Introduction

The diverse colors of natural diamond are the result of optically-active defect centers in the diamond lattice, the concentration and absorption spectra of which dictate the visual appearance of a diamond. The defect centers responsible for many diamond colors are well understood (e.g. see Ref. [1]); however the same cannot be said in the case of natural pink diamond. While the absorption band responsible for producing pink coloration in natural diamonds was first reported in 1958 [2], the nature of the defect responsible has remained unresolved over the subsequent five and a half decades [3–8].

The pink coloration arises from absorption bands centered at 550 nm and 390 nm. The depth of these bands can be reduced (the diamond can be "bleached") under ultraviolet (UV) illumination of the diamond and can be restored with longer-wavelength light (Fig. 1) [3,4,6]. Photochromism has also been noted in a number of other diamond color centers, including N–V–N (H2/H3), N–V–H, N–V, and Si–V, as well as so-called "chameleon" diamonds [9–13]. For some of these centers, the photochromism is only induced by heating or above-bandgap light, while others are purely transient and quickly relax back into a preferred state once exciting radiation is switched off. In contrast, pink diamond may be both bleached and restored optically, and the resulting color state is essentially indefinitely stable at ambient temperatures. To restore color to a bleached pink diamond by heating (thermochromism) requires temperatures of 800 °C or above [4].

Optically-activated defect centers in diamond have shown great promise, from the use of the ubiquitous N–V center in quantum-computing research to fluorescent defect-inclusive nanodiamonds being applied as biological tracers [14–16]. The remarkable optical properties of the pink color center make it a worthwhile candidate for further investigation in this spirit.

In this paper we investigate and characterize the photochromism displayed by Argyle pink diamonds. We use these observations to understand the electronic energy levels which underlie this behavior and thus the pink color center itself. We begin by constructing a general model of photochromism in terms of optical excitation of charge carriers between defect states within the electronic bandgap of diamond. This model is compared with experimental observations to explain the wavelength- and time-dependence of photochromism in natural pink diamonds.

2. Model

We model the pink diamond photochromic process as an optically-driven electronic transition between two (or more) separate defect trap states, one of which acts as a ground state for the 390 nm and 550 nm absorption bands. Bleaching of the 550 nm and 390 nm absorption bands is correlated, indicating that they share a common ground state, or at least that their respective ground states are similar in energy and strongly-coupled [6]. Following optical excitation, the color state of a pink diamond is stable if it is kept in the dark, and we experimentally estimated the time constant of color restoration for a diamond at room temperature to be on the order of 100 days. Thermally-stimulated transitions may thus be safely neglected on the time scale of the experiments conducted in this paper.

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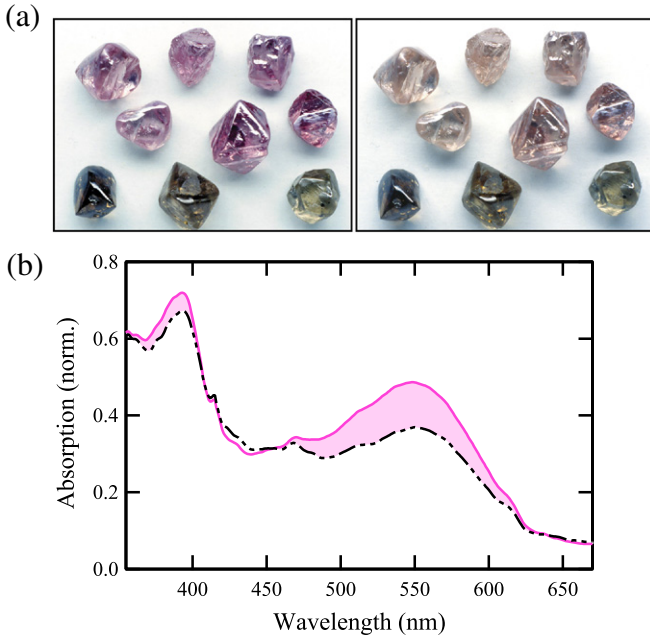E-mail address: kbyrne@physics.uwa.edu.au (K.S. Byrne).

(a)

(b)

Fig. 1. (a) Several pink and brown Argyle diamonds before (left) and after (right) UV exposure. Brown diamonds show no variation, while the pink diamonds lose much of their color. (b) The 550 nm and 390 nm absorption bands responsible for pink color in natural diamonds (pink, solid) are bleached following irradiation by UV light (black, dashed). The two absorption bands are superimposed on a long absorption tail rising towards the UV, characteristic of brown diamond coloration [1].

Such a system at its simplest can be modelled as a single species of charge carrier inhabiting one of several electronic levels, denoted here as the "pink" state p and "bleached" states b_i, positioned at some energies ϵ_p and ϵ_{bi} below a shared "excited" state e [17]. The states p and b_i are thus indirectly coupled to each other via optically-induced transitions through the intermediate excited state. Fig. 2 shows this system with the transitions marked.

If n_p and the ensemble of n_{bi} are the fractional population of centers in the original "pink" state and the "bleached" states respectively, then the transmission of light of a particular photon energy ξ through such a sample can be expressed as a typical Beer–Lambert law [18]:

$$T(\xi) \propto e^{-l\left(\varsigma_p(\xi)Nn_p + \varsigma_{b1}(\xi)Nn_{b1} + \varsigma_{b2}(\xi)Nn_{b2}\cdots\right)} \tag{1}$$

where l is the thickness of the sample, $\varsigma_i(\epsilon)$ is the optical absorption cross-section at defect i for incident light of photon energy ξ, and N is the total number density of photochromically active charge carriers.

When pumped by a monochromatic light source of photon energy ϵ, we describe the rate equations of this system as:

$$\frac{dn_p(t)}{dt} = -\omega_p(\epsilon)n_p(t) + \Gamma\left(1-\sum_i \beta_i\right)\left(1-n_p(t)-\sum_i n_{bi}(t)\right)$$
$$\frac{dn_{bi}(t)}{dt} = -\omega_{bi}(\epsilon)n_{bi}(t) + \Gamma\beta_i\left(1-n_p(t)-\sum_i n_{bi}(t)\right) \tag{2}$$

The term $\omega_p(\epsilon)$ expresses the rate for the optically-stimulated transition $p{\rightarrow}e$, which is proportional to light intensity at energy ϵ_p, and also to the interaction cross-section $\sigma_p(\epsilon)$, itself tied to the joint density of states at this energy between these two levels. Similarly, $\omega_{bi}(\epsilon)$ is the transition rate for $b_i{\rightarrow}e$, at energies ϵ_{bi} and with interaction cross-sections $\sigma_{bi}(\epsilon)$. The parameter Γ represents the rate of spontaneous decay from the excited state, with the branching term β_i representing the relative decay rate from the excited state into the ith bleached state. As shown later we use optical pump intensities

far below saturation intensity, and have thus neglected stimulated-emission terms.

For simplicity, let us initially assume only one active bleach state b with population n_b and associated pump rate $\omega_b(\epsilon)$. The solution of the system (Eq. (2)) for the population n_p will be:

$$n_p(t) = n_p(\infty) + c_1 e^{-\left(\frac{\chi+\alpha}{2}\right)t} + c_2 e^{-\left(\frac{\chi-\alpha}{2}\right)t} \tag{3}$$

where α and χ are positive parameters

$$\alpha = \sqrt{(\Gamma + \omega_p(\epsilon) - \omega_b(\epsilon))^2 + 4\Gamma\beta(-\omega_p(\epsilon) + \omega_b(\epsilon))}$$

$$\chi = \Gamma + \omega_p(\epsilon) + \omega_b(\epsilon)$$

The solution in Eq. (3) represents a double-exponential process, with the first term on the right hand side of the equation, $n_p(\infty)$, representing the steady-state color level of the diamond following long-term exposure to the pump radiation. The second term on the RHS represents a rapid exponential process as the pink state comes into equilibrium with the excited state, while the final (slow exponential) term represents the net transfer of population between the two trap states.

When Γ is much faster than w_p and w_b, c_1 tends to zero and Eq. (3) may be simplified to a single exponential process:

$$n_p(t) = n_p(\infty) - \Delta n_p e^{-\nu t}, \tag{4}$$

with

$$\nu = \frac{\omega_p(\epsilon) + \omega_b(\epsilon)}{2}$$

$$n_p(\infty) = \frac{\omega_b(\epsilon)(1-\beta)}{\omega_p(\epsilon)\beta + \omega_b(\epsilon)(1-\beta)}$$

$$\Delta n_p = n_p(\infty) - n_p(0)$$

and Eq. (1) can be simplified and expressed as

$$T(\xi) \propto e^{-lN\left(\varsigma_p(\xi) - \varsigma_b(\xi)\right)n_p(t)} \tag{5}$$

3. Experiment

3.1. Apparatus

We have verified that the shapes of the two absorption bands do not change during photochromic conversion (as is seen in Fig. 1). It is thus unnecessary to monitor the entire absorption spectrum of the diamond in order to measure the dynamic behavior of this process. In this experiment, we pass collimated light from a 545 nm light-emitting diode (LED) through a pink diamond sample, probing the depth of the 550 nm absorption band and thus the strength of the sample's
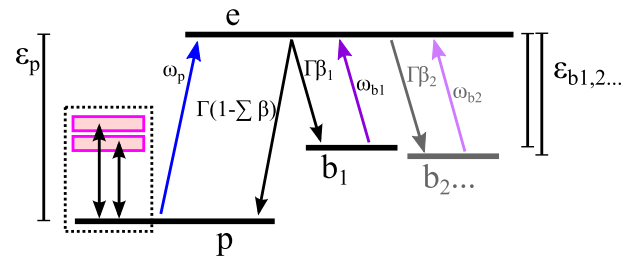

Fig. 2. Generalized model of electronic states for pink diamond photochromism. Optically driven transition rates between traps p, b_i and the excited state e are indicated by ω_p and ω_{bi} respectively; electrons may relax into each trap state according to relaxation rate Γ and splitting fractions β_i. Trap p exclusively accesses the two absorption bands responsible for pink coloration. Removal of electrons from this trap is the origin of the photochromic change.