A technique that expands on the surface luminescence imaging used in the DiamondView instrument has been developed at De Beers Group Technology, Maidenhead, UK. This provides an additional level of imaging information by way of separating prompt and delayed surface luminescence. The technique has the added benefit of quickly and easily distinguishing colorless or near-colorless natural diamond from laboratory-grown diamond. It can be applied when the identification of natural diamond is required in the study of single stones, multiples in batches, set jewelry, or in a fully automated process. The prompt and delayed luminescence characteristics of natural diamond are compared with a range of chemical vapor deposition (CVD) and high-pressure, high-temperature (HPHT) synthetic diamonds. Of significant interest are some of the less common CVD synthetic samples that have been observed in recent years. This article will summarize the luminescence observed in different diamond types, discuss its spectral characteristics, and serve as a useful reference when interpreting such luminescence images.
imaging, with techniques such as X-ray topography providing supporting evidence in more challenging cases. More recently, a set of color emission filters has been included with the DiamondView instrument to assist with some of the more challenging silicon-doped CVD synthetics that exhibit a degree of luminescence toward the red end of the spectrum, normally swamped by blue dislocation luminescence (Martineau, 2017).

To help negate the need for further time-consuming and expensive investigation, and to assist less experienced gemologists, the imaging technique employed by the DiamondView has been extended by way of hardware synchronization of the light source and camera (Smith et al., 2017), allowing camera exposures to be controlled relative to the lamp pulse with microsecond accuracy. As the temporal characteristics of diamond luminescence can be complex and the distinction between fluorescence and phosphorescence is not always clear, we use the term prompt luminescence to describe luminescence recorded at the same time as the lamp pulse, with delayed luminescence recorded after the lamp pulse.

There have been numerous “time-resolved” methods used to study the complex temporal nature of diamond luminescence. These methods can include time-gated luminescence (Khong et al., 1994; Lindblom et al., 2003; Lipatov et al., 2007), single-photon counting (Thomaz and Davies, 1978), and time-correlated single-photon counting (TCSPC) (Liaugaudas et al., 2009; Jones et al., 2020), to name a few. The method described in this article can be used to positively identify a natural type IIa or type Ia colorless diamond by accurately imaging a weak delayed luminescence having peak emission at 455 nm and a characteristic unquenched decay constant of 8.8 ms. An example of a quenched (i.e., a decrease in the luminescence efficiency and a reduction of the measured decay time) luminescence decay, which has been observed in type IIa and type Ia natural diamonds, will be shown for comparison. The absence of the blue delayed luminescence, quenched or unquenched, would indicate that a sample may be type IIb natural, unusual type Ia natural, synthetic, or simulant and would require further testing to verify its origin. The De Beers Group screened many millions of individual colorless diamonds to verify this concept, and it is this principle that is used in both the De Beers SYNTHdetect jewelry screening instrument and the second version of the Automated Melee Screener (AMS2) (figures 1 and 2) (Martineau and McGuinness, 2018).
More recently, this technique has identified a previously unknown green luminescence feature at 499 nm (Wassell et al., 2018) observable in lab-grown diamonds obtained from Gemesis Inc. (now Pure Grown Diamonds) and in silicon-containing samples sourced by Element Six that had undergone post-growth annealing.

MATERIALS AND METHODS

A selection of colorless/near-colorless natural and lab-grown polished diamond samples were chosen for this study, the details of which are listed in table 1. The samples are not an exhaustive set but were chosen to demonstrate the wide range of prompt and delayed luminescence characteristics that can be observed, and to provide a useful reference source for operators interpreting output from the SYNTHdetect instrument.

Microsecond time-gated imaging was carried out using a Teledyne Dalsa Genie Nano C2050 area-scan CMOS camera. Above-diamond band-gap excitation was provided by a Hamamatsu Photonics L7685 xenon flash lamp spectrally filtered to 190–227 nm output, with a temporal pulse width of 2.9 μs at full width half maximum. The camera and flash lamp were synchronized using the camera's internal timer, with the flash lamp signal offset by 11 μs with respect to the timer to account for the difference in latency between the two devices. Images shown represent an average of 20 individual captures. These images are at 1.5× magnification as opposed to 0.25× in SYNTHdetect for the purposes of this publication.

Room-temperature spectral data was collected by an Andor iStar DH320T-18U-E3 intensified CCD camera via a Horiba iHR-320 spectrometer, with excitation from the same source as the imaging setup. Synchronization with the flash lamp and camera was supplied by two externally generated pulsed signals offset in a similar way to the imaging setup. To record prompt luminescence, the intensifier delay was set to zero, with emission integrated over a 5 μs gate. To record delayed luminescence, the intensifier delay was set to 100 μs or more, with emission integrated over a chosen gate. Here, 40 accumulations were averaged. A simplified diagram illustrating the principle of time-gated luminescence is shown in figure 3.

Selected room-temperature delayed luminescence decay data was collected by a Horiba Jobin Yvon IBH TBX-04 thermoelectrically cooled photomultiplier

### Table 1. Diamond samples from this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Shape and Cutting Style</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Type IIa natural</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>D2</td>
<td>Green-fluorescing type Ia natural</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>D3</td>
<td>Unusual natural</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>D4</td>
<td>Weak type Iib natural</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>C1</td>
<td>As-grown nitrogen-containing CVD</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>C2</td>
<td>CVD of Chinese origin</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>C3</td>
<td>Gemesis CVD synthetic</td>
<td>Modified square brilliant</td>
</tr>
<tr>
<td>C4</td>
<td>Diamond Foundry CVD</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>C5</td>
<td>CVD of unknown origin</td>
<td>Round brilliant</td>
</tr>
<tr>
<td>S1</td>
<td>Typical HPHT synthetic</td>
<td>Round brilliant</td>
</tr>
</tbody>
</table>

Figure 3. Simplified diagram of time-gated luminescence. To acquire a delayed spectrum or a delayed image, the detector or camera is activated after a delay, which ensures that the prompt luminescence has decayed almost to zero. Switching the detector or camera on and off is analogous to the opening and closing of a gate. To detect the prompt luminescence, and reject the delayed luminescence, the detector is turned on only when the lamp is on.
module via a Horiba iHR320 spectrometer with excitation as above. Detector and flash lamp were triggered simultaneously, with channels recording both prompt and delayed luminescence in each time sweep of the multichannel analyzer. The time spacing of the channels was selected to suit the decay time being measured. After the data were accumulated, the channels recording prompt luminescence were rejected.

RESULTS

Natural Diamonds. The luminescence characteristics of a typical type IIa natural diamond are shown in the figure 4 set. The prompt luminescence (figure 4A) is dominated by blue luminescence from dislocations and is identical to that seen in the DiamondView instrument. The delayed luminescence (figure 4B) cannot be observed in DiamondView images due to the weak nature of the luminescence and the fact that it is masked by the prompt dislocation luminescence. It can be seen from the imaging that the blue delayed luminescence is not related to the blue dislocation prompt luminescence. The spectral data (figure 4C) and decay data (figure 4D) also show that it does not arise from N3 defect fluorescence. Figure 4E is an example of quenched blue delayed luminescence decay and is shown for comparison with the unquenched decay of sample D1. This blue delayed luminescence is the specific marker used by AMS2 and SYNTHdetect as a positive identifier of natural diamond, as it is not seen in synthetic diamonds.
This was confirmed in tests by De Beers Group on over 20 million individual colorless diamonds. In addition, the Diamond Producers Association ASSURE program found that less than 1% of natural diamonds do not exhibit this luminescence and would be referred for further testing (Dupuy and Phillips, 2019). At the time of writing, the origin of this luminescence is not fully understood.

The diamond in figure 5A is a predominantly “green-fluorescing” example where the green prompt luminescence is attributed to the H3 defect and the blue to the N3 defect, as shown by the spectral data in figure 5C. The spectral data further show that the delayed luminescence is not related to N3 defect fluorescence, although the delayed luminescence image (figure 5B) shows that it is predominantly in the same spatial region of the stone as the N3 luminescence, which may suggest it is related to higher aggregated states of nitrogen such as B-centers.

Diamond D3 is a slightly more unusual natural diamond in that it exhibits blue prompt luminescence (figure 6A) and a blue/green delayed luminescence (figure 6B). The green delayed luminescence component is due to the H3 defect (figure 6D). This phenomenon has been reported previously and attributed to the population of triplet states within the defect (Pereira and Monterio, 1991). In this sample, the spectral data also show a small contribution of H3 in the prompt luminescence. By extending the delay time from the microsecond range to the millisecond range reduces the fast-decaying green components, allowing the underlying blue luminescence to be observed—a feature that is available to users of the SYNTHdetect instrument. Extensive testing by De Beers indicates that ~0.5% of natural diamonds would exhibit luminescence properties such as this.

The figure 7 set illustrates a typical example of a colorless weak type Iib natural diamond, sample D4. This would show turquoise-colored long-lived delayed luminescence in the DiamondView. In figure 7A, the underlying blue dislocation prompt luminescence can be clearly seen as the long-lived turquoise delayed luminescence shown in figure 7B is gated out. This prompt luminescence would be nearly impossible to observe in the DiamondView due to the unsynchronized nature of the lamp and camera and the strong long-lived delayed luminescence, which would quickly mask the blue prompt luminescence. Indeed, a continual live feed of this prompt luminescence image is not possible in the DiamondView. Figure 7C illustrates the spectral profile, with the peak of the prompt luminescence at 425 nm and the peak of the delayed luminescence at 480 nm commonly seen in such diamonds. Due to the high resolution and higher magnification of these images, it is possible to identify this as natural diamond from the dislocation patterns in the prompt luminescence. However, in a lower-magnification system such as the SYNTHdetect, which is designed to look at an ensemble of diamonds in jewelry, the dislocation patterns may not be visible and such a diamond would need to be referred for further testing. This is due to the potential
for certain synthetic types to produce prompt blue luminescence and delayed turquoise luminescence.

CVD Synthetic Diamonds. Sample C1 is a typical as-grown CVD synthetic diamond that displays or-

Figure 6. A: CMOS image of sample D3 showing the prompt luminescence from a slightly more unusual natural diamond. B: CMOS image of sample D3 showing a more unusual blue/green delayed luminescence signal in a natural diamond. Recorded with a delay of 100 μs after the rising edge of the UV pump pulse and integrated for 30 ms. C: CMOS image showing the delayed luminescence recorded with a longer delay of 2 ms after the rising edge of the UV pump pulse and integrated for 30 ms. The green luminescence component has decayed. D: Prompt and delayed luminescence recorded for sample D3 showing both blue and green delayed luminescence. Delayed luminescence, recorded with a delay of 100 μs after the rising edge of the UV pump pulse and integrated for 30 ms, corresponds to figure 6B. The dotted line at 503 nm indicates the H3 zero-phonon line common to prompt and delayed luminescence.

Figure 7. A: CMOS image of sample D4 showing the spatial distribution of the prompt blue dislocation-related luminescence signal exhibited by a typical type IIb natural diamond. B: CMOS image showing the delayed luminescence signal exhibited. Recorded with a delay of 100 μs after the rising edge of the UV pump pulse and integrated for 30 ms. C: Prompt and delayed (peak at 480 nm) luminescence recorded for sample D4. Delayed luminescence recorded with a delay of 100 μs after the rising edge of the UV pump pulse and integrated for 30 ms.
ange prompt luminescence (figure 8A), primarily from the NV0 defect (figure 8C). An interesting effect noticed in this type of diamond is the delayed orange luminescence (figure 8B). Spectral analysis shows that this also originates from the NV0 defect. It can be concluded that the NV0 defect can experience emission from spin-forbidden transitions in a way similar to the H3 defect (Pereira and Monterio, 1991), although this discussion is beyond the scope of this article.

Diamond C2 is a commercially available CVD synthetic made in China. Figure 9A shows blue dislocation luminescence with discrete narrow bands and a weak general underlying red luminescence. Spectral data in figure 9C shows that the red prompt luminescence is predominantly from the NV0 defect. The delayed green luminescence in this example (figure 9B) is due to the H3 defect. Delayed luminescence from the H3 defect has been discussed for the natural diamond D3 (again, see figure 6). It is also a good indication that this synthetic diamond has undergone post-growth annealing, as this delayed luminescence has been previously observed in such samples that have undergone annealing at around 1700°C (Wassell et al., 2018).

Sample C3 is a commercially available CVD synthetic diamond from Gemesis that has been reported previously [Wassell et al., 2018]. At first glance, the delayed luminescence CMOS image (figure 10B) appears very similar to that of sample C2 in figure 9. However, the spectral data highlight that this luminescence, although similar in color, originates from an entirely different defect, with a zero-phonon line at 499 nm (figure 10C). This defect has been shown to be generated by post-growth annealing at around 1700°C. This sample is of interest in diamond verification, as it exhibits blue prompt luminescence from dislocation patterns in local regions (figure 10A) and could be incorrectly identified as a type IIa natural by a low-magnification system or an instru-
ment with a low-resolution camera where blue fluorescence is used as a natural identifier. Figure 10D shows the delayed luminescence decay profile for the 499 nm feature. It should not be assumed, however, that this observed decay is the decay profile for the 499 nm feature in general. Rather, it is the decay profile of the 499 nm feature in this sample. It was also suggested by Wassell et al. (2018) that prompt luminescence of 499 nm could not be ruled out due to swamping by blue prompt luminescence.

A commercially available CVD synthetic diamond from Diamond Foundry (sample C4) shows both a green prompt and green delayed luminescence (figures 11A and 11B). Again, this could be attributed to the H3 defect, but spectral data (figure 11C) show that this is a result of the 499 nm feature in both prompt and delayed luminescence.

Sample C5 is a commercially available CVD diamond of unknown origin. Figure 12A shows growth bands roughly perpendicular to the growth direction in the prompt luminescence, consistent with CVD synthesis. The spectral data presented in figure 12C show that this luminescence is predominantly from the 499 nm feature with components at 575 nm (the NV0 defect) and at 415 nm (the N3 defect), although this level of imaging does not show these defects in specific localized areas. Interestingly, the delayed luminescence seen in figure 12B does not show as prominent growth band patterns, suggesting the delayed turquoise luminescence does not form these patterns in the same way as the prompt luminescence. The spectral data show that the delayed luminescence is dominated by the broad turquoise feature with only a small level of the 499 nm feature visible. This sample also indicates that the 499 nm feature can experience both prompt and delayed emission.

**HPHT Synthetic Diamond.** Sample S1 is an example of a typical commercially sourced HPHT syn-
thetic diamond. The delayed luminescence (figure 13B) is identical to the strong long-lived luminescence that would be observed in the DiamondView. This long-lived luminescence is understood and has been reported as being interpretable in terms of a donor-acceptor recombination model (Watanabe et al., 1997). Of interest here is the prompt luminescence (figure 13A), which is a weak green/red and would normally be obscured by the long-lived luminescence in the DiamondView. This luminescence could be due to the presence of metal ions in the solvent catalyst. However, the prompt luminescence spectrum shown in figure 13C, along with the delayed luminescence, is broad and featureless at room temperature and gives little in the way of information.

This weak green prompt luminescence and strong long-lived turquoise luminescence are typical of many HPHT synthetics. They can be used as an identifying feature, as this combination of luminescence features have not been seen in natural diamond.

CONCLUDING COMMENTS
Diamond screening is becoming increasingly challenging, and organizations other than gemological laboratories, such as independent jewelers, auction houses, and pawnbrokers, are charged with this important task. Not only are more sophisticated techniques required to assist with this challenge, but the equipment must not be so complex to use and difficult to understand that diamond screening becomes an overly time-consuming and inefficient task. In this article, a selection of natural and lab-grown polished colorless diamonds has been studied using deep-UV excitation where the recording of the luminescence is synchronized with the excitation source, allowing a time-gated measurement. This technique provides a useful additional level of verification when screening
for challenging synthetics such as blue-fluorescing CVD synthetics. Although the examples contained in this article are not an exhaustive list, they should serve as a useful reference guide and knowledge base for all SYNTHdetect users when studying individual samples or screening challenging examples.

REFERENCES


