The influence of the substrate temperature and argon flow on the compositional, structural, optical, and light emission properties of amorphous hydrogenated silicon carbonitride (a-SiCxNy:H) thin films was studied. Thin films were fabricated using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD) at a range of substrate temperatures from 120 to 170°C (corresponding to deposition temperatures of 300 to 450°C) in a mixture of SiH4, N2, and CH4 precursors. Variable angle spectroscopic ellipsometer (VASE), elastic recoil detection (ERD), and Rutherford backscattering spectrometry (RBS) verified optical bandgap widening, layer densification, and an increase of the refractive index at higher substrate temperatures. The microstructure of a-SiCxNy:H thin films was determined by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The substrate temperature strongly affected the binding state of all atoms, and in particular, carbon atoms attached to silicon and nitrogen, as well as hydrogen-terminated bonds. We correlated the films’ microstructural changes to a higher species’ mobility arriving on the grown layer at higher temperatures. Photoluminescence (PL) measurements showed that the total intensity of visible light emission increased. A systematic blueshift of the centroid of the wide PL peak was observed following the increase of optical gap.

Despite reports on promising mechanical properties of SiCxNy thin films, they have not yet been well explored optically. Understanding the interdependency of light emission properties and film composition and structure requires a comprehensive study. Previously, we explored the role of CH4 and N2 gas flow21 and post-deposition thermal annealing on the PL emission, composition, and microstructure of a-SiCxNy:H22 and suggested the luminescence model for this ternary material.23 However, a full understanding of the influence of the deposition conditions on the luminescence properties of SiCxNy thin films is still lacking. To the best of authors’ knowledge, only one research group examined the PL emission from a-SiCxNy thin films as a function of the deposition temperature, albeit without any discussion of the underlying mechanism and structural evolution.24 In this contribution, we present the first in-depth analysis of the influence of deposition condition on the visible luminescence from a-SiCxNy:H thin films deposited using the electron cyclotron resonance (ECR) PECVD technique. First, we discuss the influence of the substrate temperature on the growth process, and consequently, the induced changes in the film properties, including hydrogen concentration, film microstructure, and composition. We then link the evolution of these properties to the changes of visible light emission by varying the substrate temperature. In addition, in plasma-assisted methods, inert gases such as argon (Ar) can be added to the plasma to enhance the ionization efficiency. We review the influence of Ar addition to the growth process and its consequences on the film composition and luminescence properties.

Experimental

Sample preparation.—a-SiCxNy:H thin films were fabricated using an ECR PECVD system, where reactant gases were fed into the main chamber for 30 minutes. The system was designed to feed N2 and Ar gases into the plasma region and supply CH4 and SiH4 gases downstream from the discharge zone through a dispersion ring positioned out of the plasma region close to the substrate. With a fixed
microwave power of 500 W, the stage temperature (denoted as the deposition temperatures, Td) was varied from 300–450°C, in 50°C increments, corresponding to substrate temperatures (denoted as Ts) of 120, 137, 154, and 170°C, respectively. The temperature on the substrate surface was assumed to be similar to the back side of the sample stage, where the thermocouple was placed in contact with the substrate holder. During the deposition, the plasma can increase the surface temperature of the sample to about 150°C for a deposition time of 120 minutes. For the investigated samples of this work, the “plasma on” time was set to 30 minutes, which resulted in an increase of the substrate temperature by a few tens of degrees.25

We have described further details of this deposition system elsewhere.25 Prior to the deposition, the n-type (0.01–0.03 Ω-cm resistivity) silicon wafers were cleaned with buffered hydrofluoric acid (HF) for 60 s to remove the native oxide layer while the vitreous carbon plates were cleaned using acetone followed by methanol, both using sonication for 10 min. To explore the influence of substrate temperature, four a-SiCnxNymHz samples (SiCN-300, SiCN-350, SiCN-400, and SiCN-450) were grown using identical parameters except the deposition temperature that was kept at 300, 350, 400, and 450°C, respectively. Gas flow rates of 5, 10, and 8 (±5%) sccm were used for 30% SiH4 diluted with Ar, 10% N2 diluted with Ar, and pure CH4, respectively. RBS was employed to measure all constituent elements of a-SiCnxNymHz samples (including hydrogen) as a function of deposition temperature (Td). With an increase of Td from 300 to 400°C, the concentration of hydrogen and nitrogen decreases, the carbon content increases, and the silicon content is virtually constant. At Td = 450°C, the concentration of silicon and nitrogen decrease drastically and the film becomes strongly carbon rich.

kept below 3 mTorr. The thickness, optical bandgap, and refractive index of the films were delivered by the simulation of variable angle spectroscopic ellipsometry (VASE) data using J. A. Woollam’s CompleteEASE software package. VASE measurements (Ψ and Δ parameters) of the layers were obtained through the reflectance spectra at multiple angles of incidence (55°, 60°, 65°, 70°, and 75°) in the range of UV–VIS–NIR (300–1600 nm). The room-temperature PL spectra of the samples were measured in a wavelength range extending from the region of the near-infrared (NIR) (1100 nm) to the UV (350 nm) using charge-coupled device (CCD) arrays and a 325 nm He-Cd laser (Eexc = 3.82 eV) with an optical power of 5 mW exciting an area of 2.3 mm². More details regarding the spectrometer and system response used for the correction can be found in Reference 28. The PL data recorded as a function of wavelength was first corrected with the system response and then smoothed using a Savitzky-Golay function.

### Results

**Compositional analyses.**—The combined RBS-ERD results show that the substrate temperature strongly affects the film composition. Fig. 1 shows the variation of the concentration of all constituent elements of a-SiCnxNymHz samples (including hydrogen) as a function of the deposition temperature with the corresponding experimental uncertainties. The small uncertainties are related to the use of a glassy carbon (vitreous carbon) substrate, which has an RBS signal at lower energy than the light elements in the SiCnxNymHz layer, in contrast to the commonly used silicon substrate. The values of the atomic concentrations listed in Table I indicate that an increase of Td from 300 to 400°C (T, from 120 to 154°C) decreases the nitrogen concentration.

| Sample     | Td (°C) | [H] ± 1.8 (at. %) | [C] ± 1.0 (at. %) | [N] ± 0.8 (at. %) | [Si] ± 0.4 (at. %) | d ± 0.4 (nm) | n (λ = 632.8 nm) | Mass Density (±0.07 g/cm³) |
|------------|---------|------------------|------------------|------------------|------------------|--------------|-----------------|--------------------------|
| SiCN-300   | 300     | 38               | 28               | 12               | 21               | 381          | 1.95            | 1.88                     |
| SiCN-350   | 350     | 32               | 37               | 10               | 21               | 361          | 1.99            | 2.00                     |
| SiCN-400   | 400     | 20               | 40               | 0                | 21               | 322          | 2.04            | 2.20                     |
| SiCN-450   | 450     | 12               | 57               | 9                | 20               | 289          | 2.08            | 2.85                     |
| Ar-SiCN-350| 350     | 20               | 48               | 12               | 19               | 424          | 1.98            | 2.93                     |
by about 25% of its initial value, silicon is virtually constant, and the carbon content increases by about 75%. At $T_d = 450{°}C$ ($T_s = 170{°}C$) the concentration of silicon and nitrogen reduce drastically and the film becomes carbon rich. The hydrogen concentration decreases from 38 to 12 at. % when increasing $T_d$ from 300 to 450 $°C$ ($T_s$ from 120 to 154 $°C$). The substrate temperature affects the migration of the species on the surface and their reactions.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.}

As a result, carbon is the main element substituting hydrogen in the coating layer, while nitrogen slightly decreases. The density of the sample is provided in Table I and was calculated using the atomic concentration obtained from the combined RBS-ERD measurements and the thickness given by VASE. The film density increases when $T_d$ increases from 300 to 400 $°C$ ($T_s$ from 120 to 154 $°C$), which is related to the loss of hydrogen (and subsequent thinner layers) and incorporation of a significant amount of carbon into the film. In sample SiCN-450, in contrast to the continual hydrogen loss, the film density decreases to 1.85 gr/cm$^3$, due to the abrupt decrease of the silicon content.

**Structural analyses.**—Fig. 2 presents the C 1s and Si 2p photoemission spectra and the corresponding fits of the SiCN-350 and SiCN-400 samples, where SiCN-400 (deposited at $T_s = 154{°}C$) is presented by the solid lines. The C 1s core levels are characterized by two main peaks at 283.5 and 284.7 eV assigned to C-Si and C-C bonds and a smaller shoulder at 286.2 eV attributed to C-N bonds. The Si 2p spectra contain a mix of Si-C, Si-N, and Si-O bonds positioned at 101.1, 102.0, and 103.0 eV, respectively. The presence of insignificant amounts of oxygen is due to the slight oxygen contamination in the film and the post-deposition exposure of the sample to air after performing the HF treatment.

An increase in the substrate temperature leads to an increase of Si-C and C-N bond densities and a decrease in the concentrations of C-C and Si-N bonds. In agreement with RBS results (Compositional analyses subsection), the higher reactivity of CH$_4$ at higher temperatures generates more free radicals to form carbon-related bonds such as C-N and Si-C. The decrease of the Si-N bond density can be expected from the lower nitrogen concentration in the film layer.

The IR absorption spectra of samples grown at 300, 400, and 450 $°C$ (corresponding to $T_s = 120$, 154, and 170 $°C$) are normalized to the sample grown at the lowest deposition temperature ($T_d = 300{°}C$). The evolution of the film bond structure by varying $T_d$ is particularly significant in the three regions of the IR spectrum shown in Fig. 3. The first considerable change is observed at a peak positioned at 1100 cm$^{-1}$ (Fig. 3a), with the second region of interest located at 1700 cm$^{-1}$ (Fig. 3b). Both can be assigned to carbon-nitrogen configurations.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.}

In most cases, the overlap of the C-N and C=C absorption modes makes it difficult to distinguish them.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} We attribute the enhancement of these two peaks to the formation of more C=N/C=N bonds at higher $T_d$, which was also observed by Tomassella et al.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} Fig. 3c shows the spectra in a third region, between 1900 and 2200 cm$^{-1}$, which is an overlap of Si–H stretching modes and the C≡N stretching vibration at around 2100–2200 cm$^{-1}$. A larger density of Si-H bond is observed at lower substrate temperatures due to the higher hydrogen content in the films. The increase in the substrate temperature makes the contribution of the C≡N bond around 2200 cm$^{-1}$ significantly larger. The combination of the changes of the Si-H and C≡N bonds with the variation of substrate temperature leads to the observed shift to larger wavenumbers at higher temperatures. The evolution of the bonding configuration given by IR absorption can be explained by the cross-linking of C to N atoms due to the increase of the carbon content and hydrogen loss at higher temperatures, in agreement with the discussed XPS analysis (Fig. 2) showing a larger density of carbon bonded to nitrogen at higher temperatures. It is noted that the changes of the Si-N and Si-C bonds were analyzed only using XPS measurements and their IR results are disregarded due to the large overlap of their IR bands.

**Optical properties.**—A Cauchy model was employed for the fitting of the VASE data to describe the dispersion relation giving the refractive index ($n$) as a function of wavelength ($\lambda$) and extinction coefficient ($k$) as an exponential absorption function as follows:

$$n(\lambda) = A + B/\lambda + C/\lambda^2 + D/\lambda^4$$

$$k(\lambda) = \alpha \exp[\beta (12400(1/\lambda-1/\gamma))]$$

The fitting parameters $A$, $B$, and $C$ are the Cauchy coefficients, $\alpha$ is the absorption coefficient, $\beta$ is the exponent factor, and $\gamma$ is the band edge. Only the first three Cauchy coefficients were taken into account for our one-layer SiCN$_x$ thin films\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} and the model of the silicon substrate was adopted.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} We reported more details of the analysis of the optical constants of a-SiCN$_x$N$_y$H$_z$ thin films previously.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} Figs. 4a and 4b shows the typical spectra obtained from VASE measurements at different ellipsometric angles and the fitted data delivering the refractive index and thickness from VASE data (\(\Psi\) and \(\Delta\) parameters). Fig. 4c shows an example of the modeling of a-SiCN$_x$N$_y$H$_z$ thin films for the refractive index ($n$) and extinction coefficient ($k$) as a function of wavelength ($\lambda$) and extinction coefficient ($k$) as an exponential absorption function as follows:

$$n(\lambda) = A + B/\lambda + C/\lambda^2 + D/\lambda^4$$

$$k(\lambda) = \alpha \exp[\beta (12400(1/\lambda-1/\gamma))]$$

The fitting parameters $A$, $B$, and $C$ are the Cauchy coefficients, $\alpha$ is the absorption coefficient, $\beta$ is the exponent factor, and $\gamma$ is the band edge. Only the first three Cauchy coefficients were taken into account for our one-layer SiCN$_x$ thin films\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} and the model of the silicon substrate was adopted.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} We reported more details of the analysis of the optical constants of a-SiCN$_x$N$_y$H$_z$ thin films previously.\footnote{The observed changes of the film composition can be explained by the increase of species’ mobility arriving on the surface with higher substrate temperature and the consequent changes of the surface reactions, leading to a larger incorporation of carbon and fewer hydrocarbons into the growing film.} Figs. 4a and 4b shows the typical spectra obtained from VASE measurements at different ellipsometric angles and the fitted data delivering the refractive index and thickness from VASE data (\(\Psi\) and \(\Delta\) parameters). Fig. 4c shows an example of the refractive index and extinction coefficient. Hydrogenated SiCN$_x$ thin films are virtually transparent over
Figure 3. FTIR spectra of a-SiCxNy:Hz thin films grown at different deposition temperatures. Three specific areas of interest are shown; (a) and (b) are related to the C–N/C≡N absorption modes at 1100 cm$^{-1}$ and 1700 cm$^{-1}$, respectively; (c) between 2100 and 2200 cm$^{-1}$ are associated with an overlap of Si–H and C≡N absorption modes.

Fig. 5 shows the variation of the optical bandgap along with the other parameters determined directly from VASE simulations, i.e. refractive index and growth rate, as a function of the deposition temperature. It can be observed that higher temperatures result in optical gap widening, an increase of the refractive index, and thinner layers. It’s worth mentioning that although amorphous materials contain a random network, some features of crystalline structures due to the long-range order of periodic crystal structure can still be observed.
in short range orders of amorphous structures, such as the optical bandgap ($E_{04}$).\textsuperscript{34} The values of the optical bandgap related to the localized states were determined from the absorption coefficient (deduced from VASE simulations). The concept of the direct and indirect bandgap cannot be applied to amorphous structures due to the lack of long-range order making it impossible to define a Brillouin zone. The absorption edge in amorphous semiconductors can be considered as a “non-direct” rather than due a direct or indirect bandgap as in crystalline structures. Experimentally, the optical gap of amorphous silicon-based materials is quantified using the extinction coefficient ($\alpha$) given by the extinction coefficient ($\alpha = 2n\kappa/\lambda$). Various models exist to estimate the bandgap energy from the optical absorption coefficient.\textsuperscript{35} We employed the optical bandgap ($E_{04}$), which is the energy where $\alpha$ is equal to a standard value of $10^4$ cm$^{-1}$.\textsuperscript{36} The $E_{04}$ was found to be much closer to the effective mobility gap of silicon-based compounds given by theoretical suggestions\textsuperscript{36} compared to previous definitions of the optical bandgap such as Tauc energy gap.\textsuperscript{37}

The values of the film thickness and refractive index listed in Table I show that the increase of the substrate temperature by 50°C ($T_d$ by 150°C) results in a decrease of growth rate from 126 to 96 nm/min due to the incorporation of fewer hydrogen into the film (24% film shrinkage). The refractive index, which is related to the polarization response of a material, increases with substrate temperature. According to Lorentz-Lorenz equation, two correlated quantities, the density of the film and chemical configurations, affect the polarization.\textsuperscript{38} Higher temperature induces changes in both the film mass density and microstructure through the larger density of carbon bonds in the SiC$_x$N$_y$H$_z$ layer as a direct result of the hydrogen loss and higher carbon content.

The values of the optical gap provided in Table II indicate an increase of 0.3 eV with an increase of substrate temperature by 50°C ($T_d$ by 150°C), which is a result of the competition between the hydrogen loss and the formation of carbon-related bonds. It is well known that lower hydrogen content increases the localized mid-bandgap states in the band structure, and in turn, the optical bandgap narrows. On the other hand, the rearrangement of the film atomic structure, observed by XPS (Fig. 2) and FTIR (Fig. 3), induces a higher concentration of Si-C and C-N bonds leading to optical bandgap widening. Apparently, the evolution of structure has a more profound effect on the changes of the optical bandgap compared to the other contributor to the changes of optical gap (hydrogen loss).

**Photoluminescence.**—As discussed above, the increase of the growth temperature leads to film densification and film shrinkage. The difference in the layer thickness of the samples grown at different temperatures makes it necessary to normalize the PL spectrum of each sample to the corresponding thickness. Fig. 6a shows the normalized PL emission profile under excitation using a 325 nm laser source of different SiC$_x$N$_y$H$_z$ thin films as a function of wavelength. Due to the low signal level and the noise beyond $\sim$800 nm coming from the lower sensitivity of the CCD camera in this detection range the signal in this range is noisy. The intensity and the full width at half maximum (FWHM) of the PL profiles increase due to the enhancement of the low energy tail of the PL spectra with higher substrate temperature. To quantitatively understand the changes of the overall luminescence color, the chromaticity coordinates were calculated from the PL emission spectra. Fig. 6b shows the chromaticity coordinates of SiC$_x$N$_y$H$_z$ thin films with the corresponding deposition temperatures labelled in the CIE 1931 chromaticity diagram. The values are listed in Table II. With the increase of substrate temperature of 50°C ($T_d = 150°C$), the emission color changes from orange to yellow and is accompanied by an increase of the total emission power (as determined by integration of the emission spectrum) by a factor of 6.2 (Fig. 6c). In general, all samples show very broad PL spectra covering the whole visible range. The energy of the centroid of the PL spectra increases when the bandgap increases at higher temperatures.

**Ar gas.**—Ar dilution significantly decreases the hydrogen content from 32 to 20 at. %, where the carbon content increases significantly (see Table I). In fact, the composition of Ar-SiCN-350 sample is very close to SiCN-400 sample grown whiteout Ar dilution except for the presence of lower silicon and larger nitrogen concentration in Ar-SiCN-350. The PL emission of Ar-SiCN-350 is illustrated in Fig. 7 and can be compared with that of SiCN-350 and SiCN-400 presented in Fig. 6a. The addition of Ar enhances the PL at the higher energy range in analogy to changes observed in the PL spectrum with the increase of 50°C of $T_d$ from SiCN-350 to SiCN-400.

**Discussion**

**Substrate temperature.**—The dissociation cross section of SiH$_4$ is comparable with that of common carbon sources used in CVD techniques such as C$_2$H$_2$ and C$_2$H$_6$. The energy of formation of free radicals of the more stable gases such as (CH$_3$) is higher than that of SiH$_4$ causing the dissociation of CH$_4$ to require higher thermal energy.\textsuperscript{39} The combination of the substrate temperature of about 300°C and the energetic reactants coming from plasma more likely allows breaking of Si-H bonds (3.6 eV) originating from SiH$_4$ than C-H bond (4.3 eV) from CH$_4$. The increase of the substrate temperature is in such a way that the increased number of free radicals of CH$_4$ is more chemically active with SiH$_4$ species.\textsuperscript{40} Compositional analyses verified that more carbon was incorporated into the growing layer as a result of the variation of the species’ mobility arriving on the sample surface and the resulting chemical reactions leading to the layer formation. A decrease of hydrogen and nitrogen at higher substrate temperatures and a significant increase of carbon in the resultant films were observed.

The reasons for the low hydrogen content at higher temperatures are twofold: First, the incomplete dissociation of CH$_4$ in such low substrate temperatures causes some hydrogen atoms to remain bonded to carbon atoms in the chemical species reaching the growing surface. This incorporates more hydrogen into the film layer in the form of hydrocarbon bonds. Second, at higher temperatures, weakly bound species are more likely to be incorporated into the growing film in analogy to changes observed in the PL spectrum with the increase of 50°C of $T_d$ from SiCN-350 to SiCN-400.

**Table II.** The optical band gap ($E_{04}$) and color coordinates of SiC$_x$N$_y$H$_z$ thin films, grown at different temperatures using otherwise identical deposition parameters.

| Sample   | $E_{04}$ ± 0.05 (eV) | Color Coordinates (x, y) |
|----------|----------------------|--------------------------|
| SiCN-300 | 3.36                 | (0.51, 0.46)             |
| SiCN-350 | 3.42                 | (0.46, 0.50)             |
| SiCN-400 | 3.57                 | (0.43, 0.51)             |
| SiCN-450 | 3.68                 | (0.42, 0.53)             |
Figure 6. (a) The PL spectra excited using a 325 nm laser source of as-deposited SiCxNy:Hz thin films as a function of deposition temperature. The high energy side of the spectrum is cut off at 350 nm due to the detection limit; (b) The chromaticity coordinates labelled in the CIE 1931 chromaticity diagram; (c) The PL integrated intensity indicates a strong increase with the deposition temperature.

Figure 7. The PL emission of a-Si19C48N12:H20 thin film grown using 5 sccm of Ar (0.4 mTorr) is compared with the sample grown without the use of Ar addition during the deposition.

Hydrogen-terminated bonds are less stable leading to hydrogen desorption from the growing surface. Consequently, with the increase of temperature, carbon is the element substituting hydrogen in the layer, while nitrogen decreases.

From a structural point of view, IR absorption verified the increase of the representative bonds of CN/C= N at 1100 and 1700 cm\(^{-1}\) with higher deposition temperature. The increase of C-N and C= N bonds, despite the presence of a smaller amount of nitrogen in the film, can be explained by the changes of hydrogen cyanide (HCN) and CN at higher substrate temperatures. These two emission lines were found to be the major components in the gas mixture, which lead to the relatively low concentration of C-N bonds in CVD grown thin films.41

Higher reactivity of CH\(_4\) at higher substrate temperature yields less formation of hydrogen cyanide, HCN, providing the opportunity for the formation of C-N bonds in the film.

The increase of Si-C bonds and a decrease of Si-N bonds in the film grown using higher substrate temperatures can also be correlated to the higher chemical activity of CH\(_4\) with SiH\(_4\) radicals to forming Si-C related bonds. This provides more attachment of carbon to silicon in the growing film decreasing the opportunity for nitrogen atoms to be bonded to silicon. Moreover, the Si-C bonds increase by the connection of silicon and carbon dangling bonds generated by the hydrogen desorption on the surface of the film.

Therefore, the higher reactivity of CH\(_4\) at higher temperatures not only promotes the incorporation of more carbon in the layer, but also reduces the amount of hydrogen-terminated bonds in the film, providing more cross-linking of carbon atoms in the resultant film. All induced changes in the optical bandgap, layer density, and refractive index correlate with the described process of hydrogen loss, changes of film stoichiometry, and larger density of carbon-related configurations.

We took into account the characterization results described above, for the interpretation of the changes of PL properties as a function of the substrate temperature. Huran et al.24 reported a similar PL reduction with the deposition temperature, while no details on the underlying mechanism for the changes in both shape and intensity of the PL emission were discussed. In our investigated samples, the PL peak position and intensity follow the increase of the optical gap value. This indicates that the observed PL is due to the radiative recombination of carriers in localized states at the bandtails of the amorphous alloys. Furthermore, because the luminescence is intense enough to be seen with the naked eye, the probability of non-radiative recombination in a deep defect is small due to the very small mobility of carriers in the bandtails.42 Fig. 7 shows that by an increase of T\(_d\) from 300 to 350°C, the PL peak at ∼550 nm and the PL peak at ∼675 nm become far more intense. Further increase of T\(_d\) from 350 to 400°C results in a larger contribution of the PL peak around ∼675 nm, while the PL peak at
∼450 nm remains virtually unchanged. Even further increase of $T_\text{d}$ to 450 °C induces more significant changes in the PL band positioned at ∼675 nm. The origin of this PL peak is associated with carbon-related structures and the systematic increase of this peak suggests an increase of the radiative carbon-related defects with the deposition temperature, in particular from 300 to 400 °C, which is in agreement with observed increase of carbon content given by RBS analysis. As shown in Fig. 6b the luminescence color changes through orange to yellow as the deposition temperature increases, in agreement with the increase of the relative intensity of 675 nm emission. The increase of the PL band intensity at higher temperatures can be expected from the aforementioned structural and compositional discussions where the presence of more carbon in the film leads to a larger density of carbon bonds (Si-C and C-N bonds) and consequently, an increase of carbon-related emissions. The PL peak ∼500 nm arises from nitride related defects and the decrease of this peak with increasing deposition temperature can be explained by the lower nitrogen content, as verified by XPS and RBS.

**Ar gas.—** The addition of Ar gas changes the plasma chemistry and the dissociation rate of precursors which affect consequently the film composition and bonding states of the elements in the growing layer.

The active Ar species extracted from the plasma region dissociate $\text{CH}_4$ (with higher activation energy) more effectively explaining the significant increase of carbon content in the resultant film (see Table 1). This is in agreement with the studies indicating higher conversion rate of $\text{CH}_4$ with the addition of rare gases such as Ar. Besides the higher ionization of the $\text{N}_2$ gas in the plasma and $\text{CH}_4$ near the samples surface, the kinetic energy of Ar ions can heat up the surface sample and influence the species reactions on the surface of the growing layer. It can be inferred that Ar dilution influences the film properties in analogy to the increase of the deposition temperature by 50 °C ($T_\text{d}$ by 15 °C). Both $\text{SiCN-400}$ and Ar-$\text{SiCN-350}$ samples showed higher carbon and lower hydrogen contents compared to the $\text{SiCN-350}$ sample. The hydrogen loss with Ar dilution was previously reported by other researchers for carbon films and is related to the hydrogen desorption from the growing surface at higher temperatures. The only difference between $\text{SiCN-400}$ and Ar-$\text{SiCN-350}$ is the higher nitrogen and lower silicon content in $\text{SiCN-400}$. This can be explained by higher activation of strongly bonded $\text{N}_2$ in the plasma and containing more Ar gas, which makes the amount of available $\text{N}_2$ species larger than the amount of $\text{N}_2$ species in the $\text{SiCN-400}$ sample grown with no Ar dilution. In SiCN-400 a decrease in the density of Si-N bond was observed by XPS and FTIR and nitrogen content was observed due to the competition of constant $\text{N}_2$ species with the increasing number of reactants generating from $\text{CH}_4$. In Ar-$\text{SiCN-350}$ sample, the $\text{N}_2$ radicals created in the plasma cone impacted the gas phase chemical reactions and the species arriving at the surface that ultimately leads to the incorporation of more nitrogen and less silicon in the film. With respect to the difference of the PL emission between Ar-$\text{SiCN-350}$ and SiCN-350 samples, the latter showed enhancement ∼500 nm where the origin of the PL emission was assigned to the nitrogen-related structures in the a-\text{SiC}$_x$N$_y$ thin films, which is consistent with the higher nitrogen content of Ar-$\text{SiCN-350}$.

**Conclusions**

We presented a comprehensive analysis of the influence of substrate temperature on the structure and visible luminescence emission of a-\text{SiC}$_x$N$_y$H thin films deposited using the ECR PECVD technique. The hydrogen content showed a decrease with the substrate temperature, i.e. 38 to 7 at. % for temperatures ranging from 120 to 170 °C, corresponding to the deposition temperatures of 300 to 450 °C. Carbon was the main element substituting hydrogen in the film layer, while nitrogen (and silicon slightly) decreased. XPS and FTIR analyses verified that the carbon binding states changed significantly through the formation of more Si-C and C-N/C$_2$N = N bonds. The optical properties of the a-\text{SiC}$_x$N$_y$H$_z$ thin films (PL, refractive index, and optical bandgap) were discussed in terms of the evolution of microstructure and film composition.

An increase of 50 °C in the substrate temperature (corresponding to 150 °C of deposition temperature) reduced the areal density of the layers due to the formation of denser layers and hydrogen loss. The refractive index of the films was found to increase with higher temperatures, which is due to the hydrogen loss and the subsequent more dense structure along with the formation of carbon-related phases. With an increase of the substrate temperature, the optical bandgap widened due to the more profound effect of structural changes competing with the hydrogen loss. The visible PL emission showed a systematic blueshift of the centroid of the wide peak following the increase of optical gap. These features indicate recombination between localized states in the bandgap and the systematic increase of the relative intensity of 675 nm emission with an increase of 50 °C. However, Ar dilution was found to increase the contribution of the PL band originated from nitrogen-related structures compared to the non-Ar grown samples due to the increase of nitrogen content, which coincided with the carbon enrichment.

The foregoing discussions suggest that the loss of hydrogen and higher carbon binding states are consequences of higher substrate temperature and Ar dilution, which open opportunities for a better control of the deposition conditions depending on the desired applications.

**Acknowledgments**

This work was funded by the Natural Sciences and Engineering Research Council (NSERC) under the Discovery Grants program. G.B. F. Bosco was funded by a CAPES scholarship. L. R. Tessler was funded by Unicamp/FAEPEx. The authors gratefully acknowledge Leyla Soleymann at McMaster University for valuable discussions, Lyudmila Goncharova, William Lennard, and Jack Hendriks at the Tandemtron Laboratory at Western University (London, Ontario) for their assistance with RBS and ERD measurements, and Mark Biesinger at Surface Science Western (London, Ontario) for the acquisition and primary analysis of XPS experiments.

**ORCID**

Z. Khatami https://orcid.org/0000-0001-9371-3429
P. Mascher https://orcid.org/0000-0002-8108-0334

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