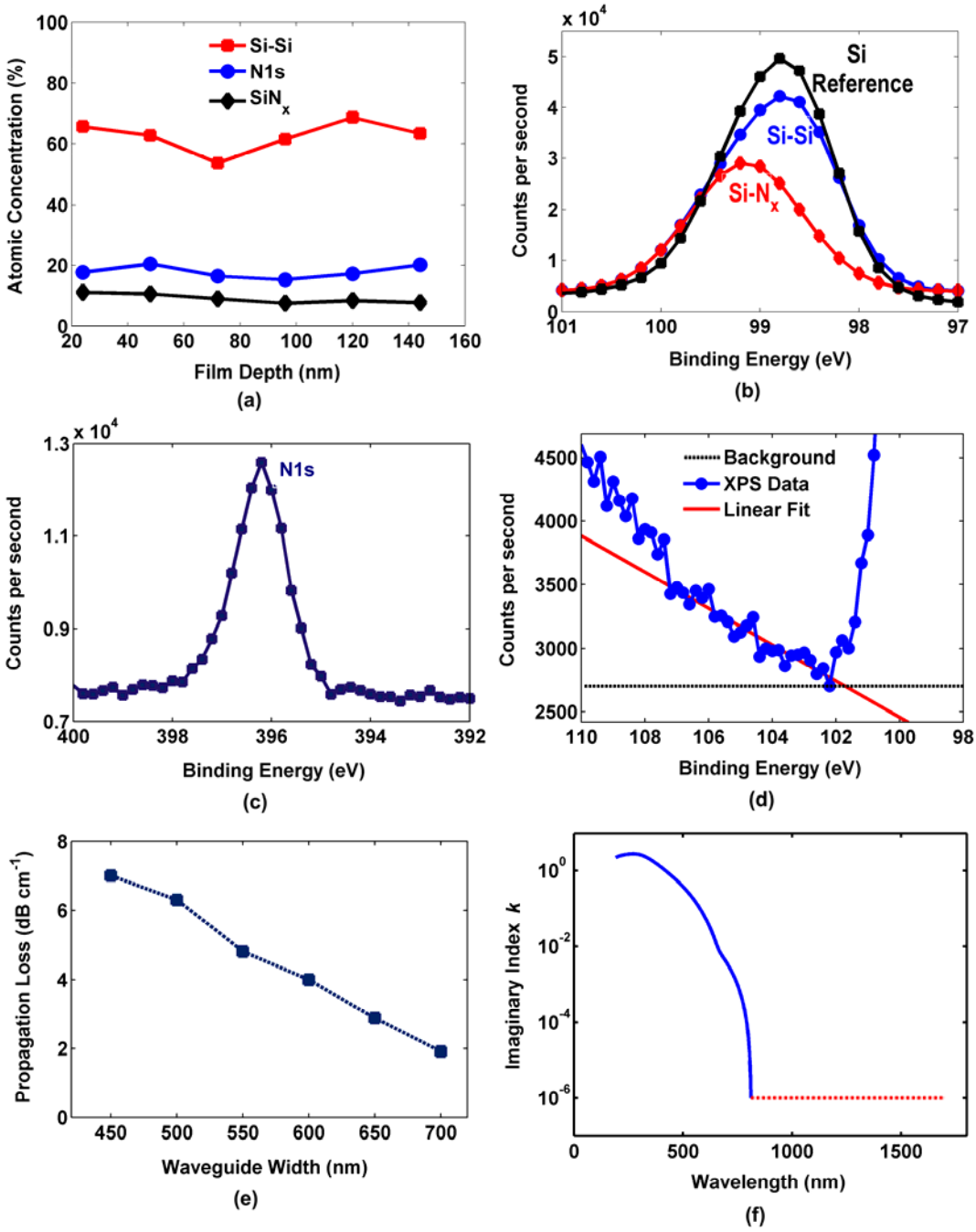
SUPPLEMENTARY FIGURES



Supplementary Figure 1. X-ray photoelectron spectroscopic characterization of the USRN film. (a) Atomic concentration of the Si-N, Si- Si and N1s bonds within the film, as a function of film depth. (b) XPS Si 2p spectra of USRN film deconvoluted into two peaks. A pure Si film is used as a reference for the Si-Si peak. (c) XPS N1s core-level spectrum of the USRN film. (d) XPS spectrograph corresponding to inelastic collisions used to extrapolate the band gap energy of the film. (e) Measured waveguide propagation losses as a function of the waveguide width with improved losses. The propagation losses decrease as waveguide

width is increased, suggesting that sidewall roughness plays a big role in the measured propagation losses. (f) Measured material loss of USRN. The lowest measurable *k* value is 10^{-6} or 0.35 dB cm^{-1}. Material loss from wavelength 810 nm to 1700 nm is below the detection limit (red dashed line).

SUPPLEMENTARY NOTE 1

Supplementary Figure 1a shows the plot of the atomic concentration of USRN taken using X-ray photoelectron spectroscopy (XPS) from a depth of 20 nm to 140 nm into the film. The measurement detects the presence of Si and N with a higher percentage of Si concentration. The ratio of Si:N is extracted to be approximately 7:3, which is close to that which was detected by energy dispersive X-ray spectroscopy. Previous characterization using EDX measurements were sufficient mainly to determine the presence of higher amount of Si compared to N in the silicon-rich nitride film and to estimate the Si:N ratio. Further characterization using XPS performed here provides a more accurate measurement on the film composition compared to EDX as it uses a monochromatic Al K-alpha X-ray source under high vacuum to obtain the film's chemical compositions and more importantly, the binding energies. By X-ray bombardment, core electrons in the film are excited and therefore freed from the nucleus attractive force. Once the electrons are in the vacuum, they are collected by an electron analyzer. The XPS spectrum is obtained by counting the number of electrons versus their binding energy.

Apart from the percentages of Si and N in the film, an important result obtained through XPS characterization is the exact binding energy of the USRN films, and determines that Si–Si and Si–N bonding did indeed occur in the film. Supplementary Figure 1b shows the XPS binding energies' narrow scan from 97-101 eV alongside a reference measurement using a pure Si film sample. Taking the Si–Si peak (98.7 eV) as a reference, USRN film is further deconvolved into two curves at 98.7 eV (Si-Si peak) and 99.2 eV. This indicates that the USRN film consists of an Si-Si peak and a second peak. As this second peak occurs at neither Si_3N_4 (101.8 eV)[1] nor SiO_2 (103.6 eV)[2] and atomic concentration (Supplementary Figure 1a) reveals presence of Si and N, we believe that this second peak is attributed to the Si-N_x bonding in the film. Furthermore, a narrow scan from 392-400 eV reveals an N1s peak at approximately 396.2 eV (Supplementary Figure 1c), which corresponds to the typical N1s peak of Si-N (Ref. 3), further evidence that Si-N bonds indeed exist in our films. The presence of Si-Si, N1s and Si-N bonds in the indicated percentages suggests that the film possesses bonds which are similar to that of stoichiometric silicon nitride films, but with a comparatively larger amount of Si-Si, thus confirming the silicon-rich nature of our films.

Energy losses observed via X-ray photoelectron spectroscopy enable the energy band gap of the silicon rich nitride film to be extrapolated[3]. Inelastic scattering from surface plasmons induced by photoexcited electrons generate an energy loss equivalent to the material's energy band gap. This reduction in kinetic energy manifests itself as a broad peak with an increased binding energy relative to the location of the characteristic bond's elastic peak. The band gap energy can therefore be derived from

the difference between the location of the elastic peak, and that where inelastic collisions are observed to occur in the XPS spectrograph. Supplementary Figure 1d shows the XPS spectrograph of our USRN film used to extrapolate the band gap energy, where the onset of inelastic collisions occurs. The intersection point between the background level of the measurement and the linear fit to the slope immediately preceding the Si-N peak represents the upshift in binding energy relative to the Si-N peak as a result of inelastic collisions. The difference between this intersection point and the Si-N peak gives us the band gap energy of the film, determined to be 2.1 eV. This band gap energy is large enough to eliminate two-photon absorption at 1550 nm, including those from Urbach tails which are characteristic of amorphous films, and places the film well above the two photon absorption edge. From Supplementary Figure 1a, it is also observed that the Si:N ratio stays relatively constant at various film depths, implying that our films are homogeneous. This property is important to ensure that the material's nonlinearity effectively interacts uniformly with the waveguide mode residing within the USRN core. Further, optical characterization of the films' *n*–*k* values has revealed that our films possess a relatively large linear refractive index of 3.1 at 1550 nm (Ref. 4), and allows for significant design freedom to engineer varying magnitudes and signs of waveguide dispersion, a feature which is important for many nonlinear optics phenomena such as four-wave mixing and optical pulse compression. The nonlinear Kerr coefficient was previously evaluated to be 2.8×10^{-13} cm^2 W^{-1} (Ref. 4).This nonlinear parameter is slightly higher than that in silicon waveguides, and two orders of magnitude larger than that in silicon nitride, silicon-rich nitride waveguides (with a refractive index ≤ 2.2) and Hydex waveguides, which when coupled with the large band gap characterized using XPS to be 2.1 eV, implies a high nonlinear figure of merit at 1550 nm.

SUPPLEMENTARY REFERENCES

1. Lee, W. J. & Kim, U. J. Characteristics of silicon nitride thin films prepared by using alternating exposures of SiH_2Cl_2 and NH_3. *J. Korean Phys. Soc.* **47**, S598-S602 (2005).

2. Ulrich, M. D. *et al*. Soft X-ray photoelectron spectroscopy of $(HfO_2)_x(SiO_2)_{1-x}$ high-*k* gate-dielectric structures. *J. Vac. Sci. Technol. B* **21**, 1777-1782 (2003).

3. Goto, T. & Hirai, T. J. ESCA study of amorphous CVD Si_3N_4-BN composites. *J. Mater. Sci. Lett.* **7**, 548-550 (1988).

4. Wang, T. *et al.* Supercontinuum generation in bandgap engineered, back-end CMOS compatible silicon rich nitride waveguides. *Laser Photon. Rev.* ***9***, 498-506 (2015).